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River Sediment Sampling and Environment Quality Standards: A Case Study of the Ravensbourne

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School of Life Sciences

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University of Westminster

River Sediment Sampling and Environment Quality Standards: A Case Study of the Ravensbourne River

Ngozi Uzoamaka Mokwe Ozonzeadi

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS OF THE UNIVERSITY OF WESTMINSTER FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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Abstract

Sediment is a major sink for heavy metals in river, and poses significant risks not only to river quality but also to aquatic and benthic organisms. At present in the UK, there are no mandatory sediment quality standards. This is partly due to insufficient toxicity data but also due to problems with identification of appropriate sediment monitoring and analytical techniques. The aim of this research was to examine the sampling different river sediment compartments in order to monitor compliance with any future UK sediment environmental quality standards (EQS). The significance of sediment physical and chemical characteristics on sampling and analysis was also determined. The Ravensbourne River, a tributary of the River Thames located in the highly urbanised South Eastern area of London was used for this study. Sediment was collected from the bed using the Van Veer grab, the bank using hand trowel, and from the water column (suspended sediment) using the time integrated suspended tube sampler between the period of July 2010 and December, 2011. The result for the total metal extraction carried out using aqua regia found that there were no significant differences in the metal concentrations retained in the different compartments by the <63µm sediment fraction but there were differences between the 63µm-2mm fractions of the bed and bank. The metal concentration in the bed, bank and suspended sediment exceeded the draft UK sediment quality guidelines. Sequential extraction was also carried out to determine metal speciation in each sediment compartment using the Maiz *et al.* (1997) and Tessier *et al*. (1979) methods. The Maiz *et al.* (1997) found over 80% of the metals in each sediment compartment were not bioavailable, while Tessier *et al*. (1979) method found most of the metals to be associated with the Fe/Mn and the residual phase.

The bed sediment compartment and the <2mm (<63µm + 63µm-2mm) fraction appears to be the most suitable sediment sample for sediment monitoring from this study.

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List of Acronyms

AA-EQS	Annual Average Environmental Quality Standards
ANZECC	Australian and New Zealand Environment and Conservation Council
AR	Aqua regia
BCR	Community Bureau of Reference
CB-TEC	Consensus based -Threshold Effect Concentration
Cd	Cadmium
CEC	Cations exchange capacity
CHN	Carbon, hydrogen, nitrogen
CIEH	Chartered Institute of Environmental Health
Cu	Copper
CSOs	Combine sewage overflows
DO	Dissolved oxygen
DOC	Dissolved Organic Carbon
DTPA	Diethylene triamine pentaacetic acid
EC	European Commission
EC-TEL	Environment Canada Threshold Effect Level
EQSs	Environmental quality standards
ERL	Effects Range Low
EU	European Union
Fe	Iron
GIS	Geographical information system
$HClO_4$	Perchloric acid
HF	Hydrogen fluoric acid
HM	Heavy metal
HNO_3	Nitric acid
H_20_2	Hydrogen peroxide
IAEA	International Atomic Energy Agency
ICP AES	Inductively coupled atomic emission spectrometry
ICP MS	Inductively coupled plasma mass spectrometry
ISQG	Interim Sediment Quality Guidelines
ISQV	Interim Sediment Quality Value

Km	Kilometre
LAS	Left after storm suspended tube sampler
LEL	Lowest Effect Level
LM1	Left monthly suspended tube sampler
LOI	Loss on ignition
MAC-EQS	Maximum Allowable Concentrations Environmental Quality Standards
mL	Milliliter
mm	Millimeter
Mn	Manganese
Ni	Nickel
NOAA	National Oceanic and Atmospheric Administration
Pb	lead
PEC	Probable effect concentration
PEL	Predicted effect level
POC	Particulate Organic Carbon
PPB	Parts per billion
PPM	Parts per million
RAS	Right after storm suspended tube sampler
RM	Right monthly suspended tube sample
RPM	Rotation per minute
RV	Reference value
SD	Standard deviation
SEL	Severe effect level
SEM	Scanning electron microscopy
SETAC	Society of Environmental Toxicology and Chemistry
SPSS	Statistical Package for Social Sciences
SQAV	Sediment Quality Advisory Value
SQG	Sediment Quality Standard
SQO	Sediment Quality Objective
SQS	Sediment quality guideline
SSA	Specific surface area
STWs	Sewage treatment works
TEA	Triethanolamine

TEL	Threshold effect level
TET	Toxic effect Threshold
TISTS	Time Integrated Suspended Tube Sampler
µg/L	Microgram per litre
UKAS	United Kingdom Accreditation Service
UKTAG	United Kingdom Technical Advisory Group
USEPA	United State Environmental Protection Agency
µm	Micrometer
WFD	Water Framework Directive
v/v	Volume by volume
XRD	X-ray diffraction
Zn	Zinc

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Declaration

The thesis and research described here are carried out by the author unless where otherwise stated.

Ngozi Mokwe Ozonzeadi

SECTION 1- Introduction/Literature review/Study area/Materials and Methods

Chapter 1
1.0 Introduction

Sediments are particulate materials consisting of various physical and chemical substances that are transported and eventually deposited at the bottom of rivers (SedNet, 2004; Brils, 2008). Fluvial sediment forms an integral and important part of the aquatic environment and plays a significant role in water quality because higher levels of contaminants are often associated with them compared to the overlying water column (Luoma and Rainbow, 2008). Sediment can act as sources of contaminants in the aquatic environment, and have been widely used to study historical contamination long after the contamination occurred (Burton, 2002). Over the years, many studies have been carried out on the concentration of contaminants in dissolved form, with less attention given to sediment related contaminants (Taylor and Owen, 2009). However, the environmental significance of sediment in water quality management has gained recognition in recent years and a focus of concern under the Water Framework Directive (WFD), which came into force in October 2000 (Brils, 2004). The Water Framework Directive (2000/60/EC) is a key part of the water regulatory framework for European Union, and a major driver for water and sediment quality (Crane, 2003). The Directive, which requires all inland and coastal water bodies to achieve good ecological status by 2015, calls for the development of environmental quality standards (EQS) for the concentration of priority substances in water, sediment and biota (European Commission, 2000; Crane, 2003; Bennion and Batterbee, 2007).

Presently in the UK, there are no mandatory sediment quality guidelines, however, the Environment Agency have developed draft UK sediment quality guidelines using the Environment Canada threshold effect level (TEL) and predicted effect level (PEL) sediment quality guidelines.

There are a number of challenges in sediment monitoring for environmental quality standards including identifying a suitable sampling technique, the appropriate sediment compartment to sample (bed, bank or suspended sediment), and ensuring the reproducibility of sampling and analytical techniques (Crane, 2003; United Nation Environmental Programme, 2006).

1.1 Research aim

The aim of this research was to examine and determine the problems associated with sampling different river sediment compartments in order to monitor compliance with any future UK sediment environmental quality standards (EQS).

1.2 Objectives

- To establish a sampling and analytical programme on a small river known to be contaminated with heavy metals.
- To study the physical and chemical characteristics of sediment collected from different sediment compartments.
- To determine if there are any differences in heavy metal concentration between sampling techniques for different sediment compartments (bed, bank and suspended sediment) by measuring the concentration of cadmium, copper, nickel, lead and zinc in the bed sediment, suspended and bank sediment.
- To determine sediment particle size, organic matter content and mineral composition that is a possible reflection of sediment characteristics that are likely to affect heavy metal concentrations in sediment
- To establish the most reproducible, economical and easy-to-use sampling and analytical methods for different sediment compartments with respect to the concentration of cadmium, copper, nickel, lead and zinc.

1.3 Scope

The scope of this research was limited to an urban region, with South East London as a focus for fieldwork for practical reasons. The pollutants considered were the heavy metals cadmium, copper, lead, nickel and zinc. Heavy metals were selected as suitable pollutants for examining different sampling techniques and compartments, and linking these to monitoring possible environmental quality standards because they were among the classes of chemicals listed in the WFD, and are ubiquitous and relatively stable in the natural environment. The heavy metals that this research was focused on were copper, cadmium, lead, nickel and zinc. This is because: (i) they are heavy metals commonly associated with the

urban environment, and (ii) there are often historical anthropogenic activities in urban river basins, such as milling and electroplating, that could release these heavy metals into water courses with potential long term contamination of sediment. Phosphorus was also investigated. This commonly occurs as orthophosphate, a reactive form of phosphorus that is capable of reacting with heavy metals in the environment to form insoluble minerals, reducing their bioavailability (Cao *et al*., 2003; 2004). However, phosphorus was not considered as a pollutant in this research. Toxicity tests on aquatic or benthic organisms were also not covered in this research.

The Ravensbourne River located in South East London which represents a typical urban river was used for this study. The detailed description of the Ravensbourne River and the sampling location are given in chapter 3.

This thesis is divided in three sections. Section 1 consists of 3 chapters: the literature review, the study area, and the sampling and analytical design. Section 2 consists of 5 chapters which describe the results of the different analytical techniques. Finally, section 3 is the conclusion and recommendations.

Chapter 2
Literature Review

2.1 Sediment sources in the aquatic environment

Sediments are formed mainly from the weathering of rocks and the erosion of surfaces (Salomons and Förstner, 1984; Horowitz, 1991; Bridge, 2009). Sediment forms an important part of the aquatic environment, and consists of complex materials sourced from different anthropogenic and natural activities (Müller and Duffek, 2001). The quality and quantity of sediment affects river quality (Salomon and Forstner, 1984; Horowitz, 1991; Brils, 2004). High concentrations of suspended sediment increases river turbidity, which results in ecological deterioration of the aquatic environment by reducing the amount of light entering the river (Greig *et al.,* 2005). The fine sediment itself can also fill up the pore spaces in gravels that would otherwise be suitable for fish spawning, subsequently reducing the concentration of oxygen (Greig *et al*., 2005; Schindler Wildhaber *et al.,* 2014). This is especially the case when the suspended sediment consists mainly of organic matter (Bilotta and Brazier, 2008). Many contaminants enter the aquatic environment in solution before being adsorbed onto the surface of sediment. Similarly, contaminated sediment can release contaminants into the water column as a consequence of changes in environmental and weather conditions (Luoma and Rainbow, 2008).

The common sources of sediment in urban areas include channel bank erosion, re-suspension of bed sediment, landslides, construction work, sewage treatment work sludge, erosion from cultivated areas and atmospheric deposition (Taylor and Owens, 2009). Urbanization has been identified as a major factor contributing to sediment production (Harper, 2006), where the estimated production of sediment in developed areas is about twice the quantity produced during the pre-development phase (Nelson and Booth, 2002). This is mainly due to the impervious surfaces and heavily modified waterways associated with urban environments compared to the more natural river flows and the more permeable surfaces found in most rural areas (Taylor and Owens, 2009). A study carried out by Collins *et al.* (2007) to investigate the mean annual total sediment delivery to all the rivers across England and Wales from various land uses in both the rural and urban environments showed that agriculture practices have the highest percentage of sediment contribution to rivers (Table 2.1). Even so, the

percentage contribution from urban surfaces is relatively large compared to their small surface area (due to various impervious surfaces associated with urban environment).

Table 2.1 The mean annual total sediment delivery to all rivers across England and Wales from various land uses

Sources of sediment	Sediment contribution (tonnes)	Percentage sediment contribution
Diffuse from agricultural sector	1,929,000	75.7
Diffuse from eroding bank channel	394,000	15.5
Diffuse from urban sector	147,000	5.8
Point source (STWs)	76,000	3.0

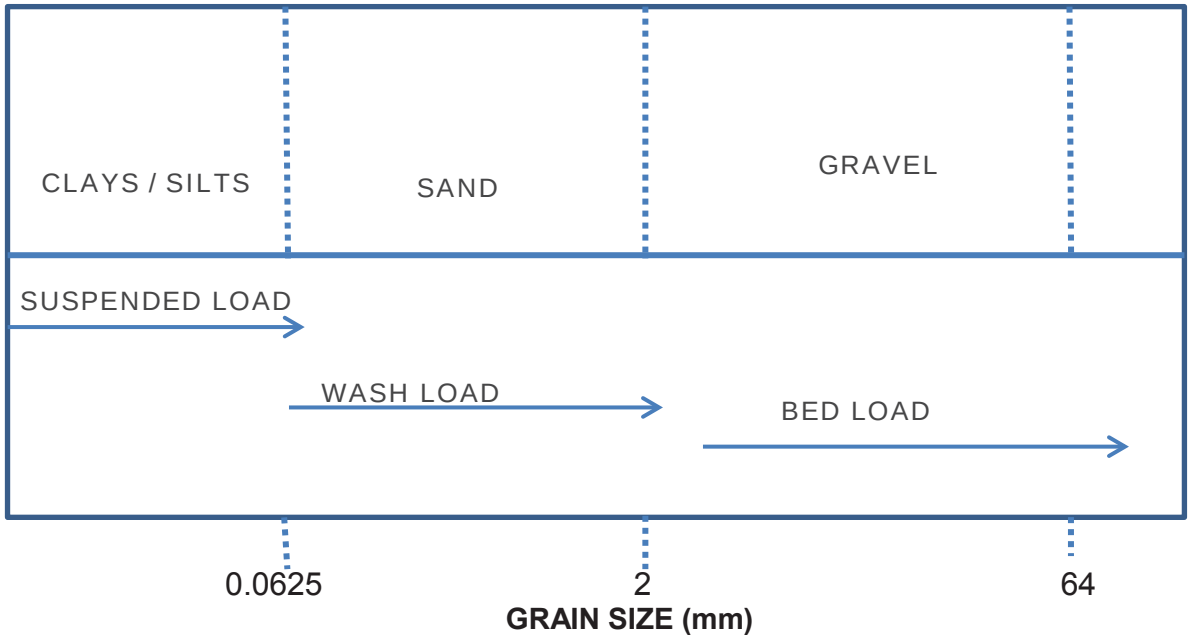
(Source: Collins *et al*., 2007)

A study by Carter *et al*. (2003) on sediment sources in the urban area of the River Aire showed that about 20-45%, 19-22% and 14-18% of sediment were from cultivated topsoil, road dust and sewage sludge respectively.

2.2 Sediment transport and deposition mechanisms in fluvial systems

The mechanism of sediment transportation is complex because of the high variability in environmental conditions such as rainfall and natural processes that are influenced by geomorphological and hydrological conditions (Salomons, 1993; Adame *et al.,* 2010). Understanding the transportation and subsequent deposition of fine sediment within rivers systems, channels and floodplains is important for sediment monitoring (Walling *et al.,* 2003). Sediments are transported and deposited preferentially in the aquatic environment depending on river velocity, particle size, climatic conditions, land use, hill slope and channel gradient (Foster and Charlesworth, 1996). The river velocity often varies at different points within a given river system, and also within a single cross section, and this can affect the grain size transported and sediment deposition rate. It is a major reason for collecting sediment samples from different points (subsampling) within a river system in order to assess local variability.

Sediments in fluvial systems are transported either as bed load (for coarse bed sediment) or as suspended load (for fine sediment), and it is widely accepted that higher proportions of sediments are transported during periods of high discharge such as a flood event (Salomons and Förstner, 1984; Petts and Foster, 1985; Salomons, 1993). Sediment transportation occurs either as suspended solids (suspended load) or movement along the bed (bed load) (Figure 2.1). Fine (<2mm) grains are mainly associated with the suspended load while larger grains are associated with the bed load (Figure 2.1).



(Adapted from Wilcock *et al.,* 2009)

Figure 2.1 Grain sizes associated with bed load and suspended load

The size, surface area, and chemical composition of the bed, bank and suspended sediment are important factors for setting sediment environmental quality standards since they are all likely to influence the adsorption and binding of contaminants to the sediment (Zhao *et al.,* 2010)

2.2.1 Suspended sediment transportation

The fine sediment (silt and clay) load is mainly transported in rivers in suspension, and the concentration of suspended sediment transported is largely dependent on water velocity (Walling *et al.,* 2000). At low river flow, sediment particles are deposited on

river beds and channels. Likewise, during high velocity flow when bottom sediments are disturbed, re-suspension and remobilization of previously deposited sediment occurs (Petts and Foster, 1985; Lenzi, 2010). This results in the transportation of sediments to new locations (Scholes *et al*., 2008). Suspended sediments found in the downstream courses of rivers are reported to be finer than those found in the upstream sectors, mainly due to the preferential deposition of the coarser particles in the upstream sectors (Lambert and Walling, 1987). Fine grained sediments are mostly transported as flocculated particles (Droppo, 2001). The quantity of suspended sediment transported in a river is a factor of the sediment source, the mechanism of transportation and the river velocity (Goodwin *et al.,* 2003).

2.2.2 Bed load sediment transportation

Bed sediment transportation in rivers is a complex process. Bed load describes the fluidic movement of sediment along the river bed or stream channel (Einstein, 1950; Wilcock *et al*., 2009). Bed-load transportation in rivers provides the relationship between fluid properties and the materials that govern river-channel morphology (Gomez, 2006; Wilcock *et al*., 2009). Wilcock *et al*. (2009) described the transportation of bed load in a river system as an intermittent, random and spatially variable process. Different formulae such as the Meyer-Peters, Einstein, du Boys, and Nielsen formulae have been used to predict the rate of bed sediment transport (Chanson, 1999). The prediction of bed sediment transport using formulae is beyond the scope of this research.

The basic modes by which bed sediments are transported include saltation (irregular jumps and bouncing movement), rolling and sliding (Petts and Foster, 1985; Chanson, 1999; Wilcock *et al,* 2009). The transportation of bed sediment in rivers is governed by the sediment size, particularly the locally available particle size at the bed surface (Gomez, 2006). Smaller particle sizes require less energy to transport compared to large grain sizes (Wilcock *et al.,* 2009) and are unlike gravel sediments which are immobile most of the time. Even during periods of increased velocity resulting from rainfall or storm events, only partial transportation of gravel sediment occurs most of the time (Haschenburger and Wilcock, 2003). The fine grains (<2mm) are the sizes

that are predominantly transported, usually being transported over the immobile gravel bed.

2.3 Sediment particle size

Grain size is the most important factor affecting sediment chemical characteristics (Horowitz, 1991; Baptista Neto *et al.,* 2000; Lin *et al.,* 2003). Sediment consists of a heterogeneous mixture of different particle sizes in the bed, banks and in suspension which originates from different sources. These differences in particle size can result in significant differences in chemical characteristics, particularly in the bed and suspended sediments, even over short distances (Horowitz and Elrick, 1987). The different sizes of sediment are given as clay < 2μm; silt - 4μm to <63um; sand- 63um to <2mm, gravel - 2mm-64mm; cobbles - 64um to 256mm, and boulders - >256mm (Wilcock *et al.,* 2009). Sediment particle size and surface area are key factors affecting the concentrations of heavy metals transported by sediments. Sediments are mainly transported as fine (<2mm) particles, and are the major transporters and sinks for contaminants such as heavy metals (Hudson-Edwards, 2003; Owens *et al.,* 2005). The clay and silt fraction (<63μm) absorbs and retains higher concentrations of heavy metals compared to the larger fractions and the dissolved concentration retained in the overlying water (Luoma and Rainbow, 2008), however, high concentrations of heavy metals have also been reported in sand fractions (>63μm) (Lin *et al.,* 2003). Sediment particle size has also been reportedly used to trace heavy metal sources, although the concentration of metals decreases as sediments move away from the source due to dilution by other pristine sediments (Salomons and Förstner, 1984; Horowitz, 1991; Miller, 1996).

2.4 Heavy metals and phosphorus in fluvial sediment

Heavy metals are defined as those elements with an atomic density greater than 6g cm^{-3} (Yirgu, 2011). Some heavy metals such as cadmium, nickel and lead are among the pollutants on the priority substance list under the Water Framework Directive (European Commission, 2001), and sediments constitute the major pathway by which these contaminants are transported to and by rivers (Chahinian *et al*., 2012). The behaviour of heavy metals in the fluvial environment is centred on factors such as their sources, sediment size and means of transportation, the presence of other

compounds, river characteristics and weather conditions such as rainfall. The major challenges related to heavy metals in the fluvial environment are that they are persistent, non-degradable, bio-accumulate in aquatic organisms, and can be integrated into food chains by biomagnification (Förstner and Wittman, 1981; Hardman *et al*., 1993; Ahdy and Khaled, 2009). The major sources of heavy metals in the urban aquatic environment are from anthropogenic sources such as zinc from automobile tyres and galvanised surfaces, and nickel from batteries and paints. Phosphorus is naturally present in the fluvial environment from the weathering of rocks and erosion of river banks as well as from anthropogenic sources such as fertilizers (Withers and Jarvie, 2008). Phosphorus reacts with metals to form insoluble complexes such as cadmium phosphate $Cd_3(PO_4)_2$, copper sulphate $Cu_3(PO_4)_2$, nickel phosphate ($Ni_3(PO_4)_2$), lead phosphate ($Pb_3(PO_4)_2$) and zinc phosphate ($Zn_3(PO_4)_2$), potentially affecting the bioavailability of the metals (Cao *et al.,* 2003; 2009).

2.4.1 Sources of heavy metals and phosphorus in the aquatic environment

Heavy metals are released into the aquatic environment from point sources such as sewage treatment works, industrial effluent and landfill sites**,** and from diffuse sources such as the weathering of rocks, erosion of bank surfaces, atmospheric deposition, sewer misconnections, road run-off and the re-suspension of contaminated bed sediment (Horowitz, 1991; Holt, 2000; Gozzard *et al*., 2011). Common sources of heavy metals in most urban rivers are mainly from historical anthropogenic activities such as milling, paintworks, power stations and ship building, while present sources are mainly from sewage treatment works, municipal waste and road run-off. Heavy metals are present in the aquatic environment either as dissolved ions or associated with sediment particles (Horowitz, 1991; West and Nurnburg, 1988). The concentration and form in which these heavy metals are released to water varies with their sources (Tack and Verloo, 1995). The most common anthropogenic sources of phosphorus in rivers are from runoff from agricultural land and cultivated surfaces, municipal waste water and combined sewer overflow (Edwards and Withers, 2008; Withers and Jarvie, 2008; Taylor and Owens, 2009). Some heavy metals like copper, zinc and nickel are essential to aquatic life in small quantities, but are toxic at high concentrations depending on their bioavailability, and on the presence of and reaction with other contaminants (Muyssen *et al.,* 2004). There are a variety of common urban

sources of the selected heavy metals (Cd, Cu, Ni, Pb and Zn) and each element has significant environmental impacts (Table 2.2) that have been mapped against the potential metal sources identified in the Ravensbourne catchment which was selected for study.

Table 2.2 Sources and environmental impact of selected heavy metals

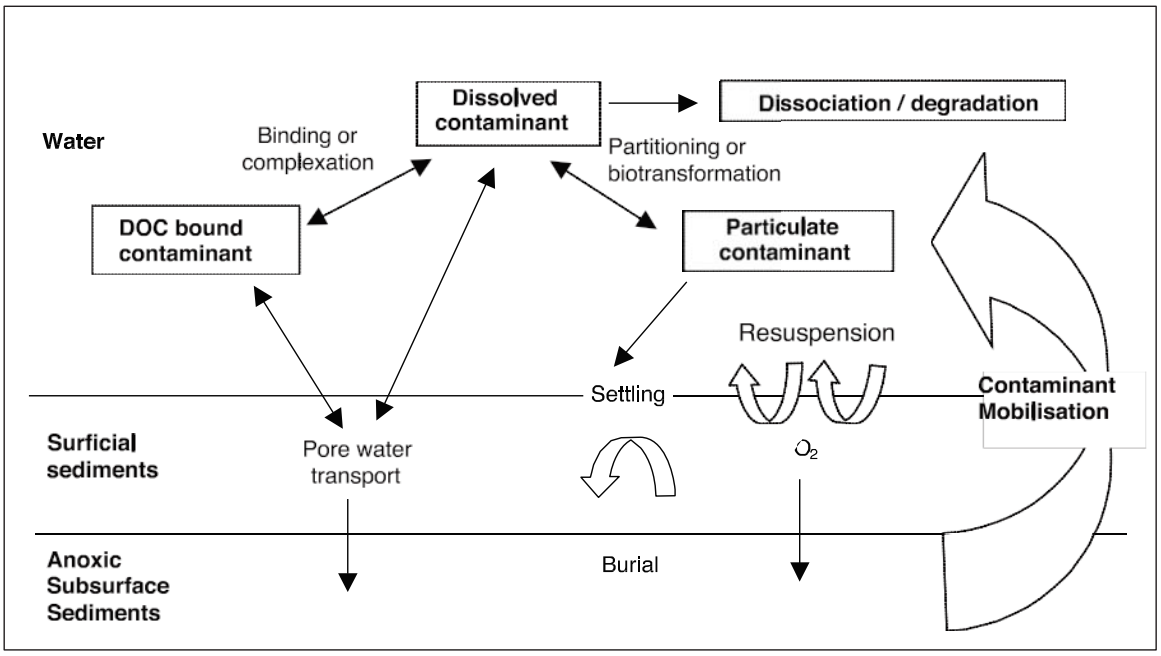
Heavy metals	Sources of pollution in Ravensbourne River	Advantages to aquatic organisms	Bioavailability to aquatic organisms	Environmental impact on aquatic organisms
Cd	The general sources of Cd is in zinc and aluminium production, and in the manufacture of iron and steel (Environment Agency, 2009b). Major sources of Cd in Ravensboure River are likely to be from Fox electroplating company (located in Sydenham) and cigarette litters(Baek and An, 2010)	It is known that cadmium can be toxic in aquatic organisms (Eisler, 1985).	Cd bioavailability increases at low pH (<5) and high dissolved oxygen 8 ± 1 mg DO l^{-1}) (Spry and Wiener, 1991, Atkinson *et al.,* 2007). Cd bioavailability decreases with increasing water hardness.	Brook trout and channel catfish are among the most sensitive group to cadmium in fresh water, at concentration between 0.47 to 5.0ppm (parts per million). Decreased growth, inhibited reproduction, and alteration in fishes population has been reported (Eisler, 1985; Spurgeon *et al.,* 2006).
Cu	Sewage treatment, tyre wear and brake emission from vehicles transportation in road run-off after rainfall, and from waste incineration (Davis *et al.,* 2001).	Cu is a micronutrient that supports growth and development in most aquatic organisms.	Low salinity and temperature (>25^{0}C) increases Cu bioavailability, toxicity is linked mainly to the dissolved cupric ion (Cu^{2+}) (Eisler, 1998a). Bioavailability decreases with increasing water hardness and high pH.	Elevated concentrations of Cu are tetratogenic (Birge and Black 1979) and cause gill damage in fishes such as the rainbow trout (Hodson *et al.,* 1979; Reid and McDonald 1991). It also interferes with the transportation of oxygen and energy metabolism in fishes (Eisler, 1998a).
Ni	Nickel batteries, tobacco, household waste from the use of nickel coated cutlery, and from pigment (Cempel and Nikel, 2006; Environment Agency, 2009c).	Nickel is an essential micronutrient for the growth and development of aquatic and benthic organisms (Eisler, 1998b).	High water temperature (>25^{0}C) increases Ni bioavailability and toxicity (Eilser, 1998b). Ni bioavailability decreases with increasing water hardness (Markich *et al.,* 2001).	Some symptoms of nickel poisoning in fishes include rapid mouth and opercular movement (Khangarot and Ray, 1990), blood hypoxia (deprivation of oxygen supply), alteration of gills structure and death ((Ellgaard *et al.,* 1995), rising level of lactic acid and blood sugar (Ghazaly, 1992).
Pb	Acid-lead batteries and lead piping in houses.	It is know that Pb is toxic at low concentration (30mg/kg dry weight of sediment) and has no known biological function in aquatic biota.	Bioavailability decreases in hard waters (Eisler, 1988) and as pH increases. Bioavailability increases with high water temperature (>25^{0}C) low pH (<5), and after prolonged exposure	Water borne lead (Pb^{2+}) is the most toxic form in the aquatic environment. Pb affects reproduction, survival rate and inhibits growth in vertebrates and invertebrates (Eisler, 1988).
Zn	Man-made emissions due to iron and steel production, tyre wear from road transport and waste incineration (Cempel and Nikel, 2006).	Zn aids neurotransmission in the brain of fish (Smeets *et al.,* 1989).	High levels of toxicity and bioavailability occurs at low pH (<5) and elevated temperatures (>25^{0}C) (Weatherley *et al.,* 1980).	High concentration damages the gills of fishes and disrupts gas exchange at the gill surface (National Academy of Science, 1979), osmo- regulatory failure, low oxygen tension in arterial blood, (Spear 1981). It also causes changes in growth and reproduction (Eisler, 1993).

2.4.2 Sediment/metal chemistry

Fluvial sediment plays a major role in the transport and recycling of heavy metals in river systems (Salomons and Förstner, 1984; Peng *et al*., 2009). Heavy metal cations are strongly attracted to the negative charge of sediment particles. This is a major reason why higher concentrations of heavy metals are associated with particulate matter than the water in river systems. The characteristics of heavy metals in the fluvial environment are largely dependent on physical and chemical processes (Salomons and Förstner, 1984; Salomons *et al.*, 1987; West and Nurnburg, 1988). Some of the physical factors affecting heavy metal chemistry are sediment particle size, surface area, specific gravity, surface charge and porosity. Heavy metals in aquatic sediment undergo different reaction to form soluble and insoluble metal complexes depending on the river characteristics such as pH, temperature and dissolved oxygen, and weather condition such as rainfall and temperature (Soares *et al.,* 1999; Atkinson *et al*., 2007).

2.4.3 Metal speciation and bioavailability in the aquatic environment

The bioavailability of metals is a decisive factor to be considered in the development of sediment quality guidelines and standards (Horowitz, 1991; Ankley *et al.,* 1996; Filgueiras *et al*., 2002). It is widely accepted that the total concentration of metals in dry weight sediment is not an indication of the toxic effect on aquatic organisms; a harmful effect is only implied if the metals are readily bioavailable (in solution when ingested by benthic organisms) (Luoma and Rainbow, 2008). The transportation of contaminants in sediment occurs mainly from the disturbance of bed sediment arising from natural and anthropogenic activities or from changes in the characteristics of the overlying water (Nriagu, 1990; Petersen *et al.,* 1997; Atkinson *et al.,* 2007). Contaminants (heavy metals) released from sediment are usually transported between the water (dissolved) phases and sediment (oxic and anoxic sediment) depending on the physico-chemical properties of the water column (Figure 2.2). Dissolved oxygen is an important factor in metal remobilization (Figure 2.2), during low dissolved oxygen, an increase in oxygen level in sediment by sediment disturbances results in metals being released into overlying water (Atkinson *et al*., 2007).



(Source: Eggleton and Thomas, 2004)

DOC- dissolved organic carbon

Figure 2.2 Transport and transformation of contaminants in sediment

The mobility and bioavailability of heavy metals trapped in sediment is dependent on the chemical form in which they are associated with sediment (Bradley, 1984; West and Nurnburg, 1988; Strom *et al.,* 2011). The geochemical phases of sediment such as carbonates, iron and manganese oxides, organic matter, sulphides and clays scavenge heavy metals and constitute the main binding sites for metals in sediment (Tessier and Campbell, 1987; Ankley *et al.,* 1996; Yu *et al.,* 2001). These binding phases sequester heavy metals through processes such as adsorption onto fine particles, precipitation of heavy metal compounds e.g. metal phosphates, co-precipitation with iron and manganese oxides, association with organic matter and incorporation in crystalline minerals (West and Nurnburg, 1988; Horowitz, 1991; Rodrigues and Formoso, 2006). Various researchers have shown that Fe/Mn oxides and organic matter effectively bind metal in oxidized sediment (Eggleton and Thomas, 2004). The mobility and the likely causes of metal mobility in the different sediment phases are described (Table 2.3)

Table 2.3 Relative mobility and availability of trace metals

Metal species and association	Mobility	Cause of mobility
Exchangeable (dissolved) cations	High	Changes in major cationic composition (e.g. estuarine environment) may cause a release due to ion exchange
Carbonate	High/ medium	Changes in river pH especially at low pH many metals go into solution at low pH.
Metals associated with Fe-Mn oxides	Medium	Changes in redox conditions may cause a release but some metals precipitate if sulphide mineral present is insoluble
Metals associated with sulphide minerals	Medium /high	With time, decomposition/oxidation of organic matter occurs, oxidation of sulphide minerals leads to release of metals
Metals fixed in crystalline phase	Low	Only available after weathering or decomposition

(Source: John and Leventhal, 1995)

The pH is the most important factor that controls the behaviour of heavy metals in the aquatic environment (Gabler, 1997; USEPA, 2007). River pH plays a major role in the solubility of metals in the aquatic environment by increasing or decreasing the ability of clay minerals, iron and manganese, and organic matter to sequester heavy metals (Förstner et *al*., 1994; Ho *et al*., 2012). At low pH values (between 1-5), heavy metal cations compete with hydrogen ions for binding sites, releasing more heavy metal ions into solution (Förstner and Wittman, 1981; Tessier and Campbell, 1987). However as pH increases (pH >5), there are less hydrogen ions to compete with heavy metals, more heavy metals bind to sediment, making them less bioavailable (USEPA, 2007). An increase in river temperature increases biological processes such as bioturbation, and decreases the level of dissolved oxygen. As a result of bioturbation or physical disturbance of bed sediment from natural activities such as tidal movement or from anthropogenic activities such as fishing or wading, heavy metals are remobilized, metal sulphides are oxidized and sequestered metals are released back into the water column making them bioavailable (Simpson *et al.,* 1998; Eggleton and Thomas, 2004; Beck and Sañudo-Wilhelmy, 2007). An increase in

oxygen levels increases the formation of metal oxides such as iron oxides in the sediment-water interface that is capable of sequestering metals out of solution or water column (Salomons and Förstner, 1984; USEPA, 2007, Luoma and Rainbow, 2008).

Manganese oxides occur either as coatings on minerals or as suspended matter and play a significant role in the distribution of metals in sediments due to their ability to sequester heavy metals (Förstner and Wittmann, 1981; Hudson-Edwards, 2003). Their sorption abilities have been attributed to their large surface area and strong negative surface charge. Hudson-Edwards (2003) has shown that the affinity of Mn oxides for metals increases in the order Ni<Zn<Cu<Pb. Sulphate also occur naturally in the environment and reacts with metal to form metal sulphates which are usually in a dissolved state. However, sulphates are reduced under anoxic conditions to form insoluble metal sulphides such as zinc sulphide (ZnS), cadmium sulphide (CdS), copper sulphide (CuS), lead sulphide (PbS) and nickel sulphide (NiS), which are not bioavailable and are stable over long periods of time (Salomons, 1993; Simpson *et al.,* 1998; USEPA, 2007). Dissolved oxygen levels decrease as organic matter increases due to biological oxygen demand (BOD) as microorganisms' uses oxygen to break down organic matter.

2.4.4 Determination of heavy metal bioavailability by selective chemical extraction

It is widely established that total metal analysis does not give an indication of metal mobility, fate, bioavailability and environmental toxicity (Ahnstrom and Parker, 1999; Sutherland and Tack, 2003; Chen *et al.,* 2010). Sequential extractions are commonly used to study the geochemical distribution and mobility of metals in sediment (Tessier *et al.,* 1979; Maiz *et al*., 1997; Alborés *et al*., 2000). Sequential extraction methods have been described as ''operationally defined'' because the amount of heavy metals extracted is dependent on the extracting solution and extraction methodology used (Hall *et al.,* 1996 Pueyo *et al.,* 2001; Hlavay *et al*., 2004). Thus measured metal concentration can vary significantly with extraction method. Heavy metals are extracted starting with the most mobile fraction, which is usually the exchangeable phase. The various geochemical phases extracted for heavy metals are the exchangeable (influenced by changes in ionic composition), carbonate bound

fraction (susceptible to changes in pH), metals bound to Fe and Mn oxides phase (susceptible to anoxic conditions or low redox values e.g. <-30mV), organic matter bound phase (susceptible to oxidizing conditions), and the residual phase (held within the crystal structure of minerals) which can only be released by strong acids such as HF (Tessier *et al.,* 1979; Zimmerman and Weindorf, 2010).

Several experimental procedures are documented for sequential extractions; however, the Tessier *et al.* (1979) sequential extraction process is the oldest and most widely applied method (Zimmerman and Weindorf, 2010). The major disadvantage of sequential extraction methods is the time it takes to complete a set of experiments and the possibility of re-adsorption during extraction (Alborés *et al.,* 2000). The time ranges for some of the sequential extraction methods include: Tessier *et al.* method - 17.5hrs; Community Bureau of Reference (BCR) method – 51hrs; Maiz *et al*.method - 6hrs; Galan *et al.* method - 14.5hrs; and Geological Society of Canada method - 21.5hrs (In Zimmerman and Weindorf, 2010). As an operationally defined experiment, the comparison of results between different sequential extraction methods is difficult due to the differences in extracting solutions and their concentrations, different treatment time and temperature and the different speciation phases (Filgueiras *et al*., 2002).

2.5 The impact of analytical methods on metal concentration

The lack of standardization in analytical techniques is one of the drawbacks in setting sediment quality guidelines **(**Alborés *et al.,* 2000; Peng *et al*., 2004; Zimmerman and Weindorf, 2010**)**. Like the sequential extraction experiments, various laboratory methods have been used in total metal extraction analysis. However, for the total metal analysis, hydrofluoric acid (HF) acid, used in combination with other acids, is the most widely adopted technique (Balcerzak, 2002; Chen and Ma, 2007). Some of the most commonly used acids in combination with HF include perchloric acid ($HClO_4$), nitric acid (HNO_3), sulphuric acid (H_2SO_4), and hydrochloric acid (HCl) (Chen and Ma, 2007). Some examples of the HF mixtures include HF/$HClO_4$/HCl (Tessier *et al.,* 1979), HNO_3/HF/HCl (Duzgoren-Aydin *et al*., 2011) and HNO_3/H_2O_2/HF (Wang *et al.,* 2004). HF is a toxic and very corrosive acid; however it is the most effective in complete digestion of geological

and complex sediment materials compared to other acids (Balcerzak, 2002). HF digests silicate minerals, and the measured metal concentration will vary with geological source of the sediments and may not accurately reflect pollutant load (Wong *et al.,* 2006). The use of less toxic acids such as aqua regia ($1HNO_3$:3HCl) is gaining recognition in recent years, primarily because it is less toxic than HF (Environment Agency, 2006; Sakan *et al.,* 2011). Aqua regia, however, does not result in complete mineral dissolution and is sometimes referred to as a pseudo-total extraction method, but aqua regia is likely to give a more accurate reflection of metal pollutant load (Sastre *et al.,* 2002).

2.6 Sediment sample preparation

One of the objectives for this study is to establish a suitable preparation and analytical method for sediment heavy metal analysis that might provide the basis for a standard technique (see Chapter 3). Various methods of sediment sample preparation such as sediment drying and sediment sieving have been used for monitoring sediment samples.

2.6.1 Sediment drying: Sediment samples can be air dried, oven dried or freeze dried depending on the chemical analysis to be carried out. Air drying of sediment allows a large amount of sediment to be dried simultaneously, but it is usually a time consuming process (Mudroch and Azcue, 1995). Freeze drying is best for analysis involving organic or volatile pollutants because contaminant loss by evaporation is minimal (International Atomic Energy Agency, 2003; SedNet, 2004b; Förstner, 2004). A major disadvantage of freeze drying is that the freeze drying units are expensive (International Atomic Energy Agency, 2003; Claussen *et al.,* 2007). Oven drying is fastest method of drying sediment and the most commonly used method of drying sediment for the determination of inorganic contaminants such as heavy metals (Förstner, 2004). The standard temperature that is frequently used is 105^0C until constant weight is achieved. A major disadvantage of oven drying is the formation of hard aggregates of sediment (International Atomic Energy Agency, 2003).

2.6.2 Sediment sieving: Sediment consists of heterogeneous materials of various particle size and composition, and sieving is the most commonly used method in

separating sediment particle size. There are no standardized methods for sieving, however, wet sieving and dry sieving are the commonly used methods for separating different sediment particle sizes (Giuliano *et al.,* 2007; Goossens, 2008). Although laborious and time consuming, wet sieving is sometimes recommended for studies on heavy metals concentrations in different sediment size fractions mainly because it can separate aggregate particles or smaller particles attached to the surface of larger particles (Simpson *et al*., 2005). Dry sieving is a faster method of separating particle size compared to wet sieving and widely used in various soil and sediment studies.

2.7 Environmental quality standards (EQSs)

Throughout the world, environmental quality standards are used to assess the chemical quality of water bodies with the aim to protect the environment from deterioration (Comber *et al*. 2008). Monitoring environmental quality and sampling are central to implementing and enforcing EQSs. Environmental quality standards have been used for over 30 years, and the processes and methodologies used to derive these standards have been constantly reviewed (Zabel and Cole, 1999; Wenning *et al*., 2005). The difficulties in setting sediment quality standards are mainly attributed to the variability in river basin characteristics and sediment characteristics, soil geomorphology, variations in benthic and aquatic organisms and their responses to heavy metal toxicity, and sampling techniques. It is widely accepted that the science of sediment chemistry and bioavailability is inadequate for the development of sediment quality standards; hence the need for more science based guidelines (De Deckere *et al.,* 2011).

Item 7 of article 16 of the European Water Framework Directive requires the submission of proposals by the Commission for the quality standards on priority substances that are applicable to surface water, sediment or biota (European Commission, 2001). The WFD is now the major driving force for EQSs in the aquatic environment in the UK and other EU countries. The WFD defines an EQS as *"the concentration of a particular pollutant or group of pollutants in water, sediment or biota which should not be exceeded in order to protect human health and the environment"* (European Commission, 2000; Lepper, 2002).

EQSs are expressed differently for acute (short term) and chronic effects (long term) on organisms. Chronic effect concentrations are described as the maximum concentration at which no adverse effect occurs when an aquatic environment is exposed to a pollutant over a long period of time and are measured against annual average concentrations. The maximum allowable concentration is the highest concentration over a short period (short term peak concentration) above which acute effect is expected to occur (Lepper, 2005). The existing EQS for fresh waters are based on acute and chronic toxicity laboratory test data available on aquatic taxa such as algae or macrophytes, arthropods, molluscs and fish (Lepper, 2002). The annual average EQS for a list of 33 priority substances in surface waters, which includes cadmium, nickel and lead, is set out in the Daughter Directives on priority substances (DIRECTIVE 2008/105/EC) (European Commission, 2008).

The Environment Agency has listed three types of substances/pollutants for which environmental quality standards are to be developed under the WFD. They include the priority substances and priority hazardous substances, specific named pollutants and physico-chemical pollutants (UKTAG, 2008a). Priority substances and priority hazardous substances are the most polluting substances that threaten human life, while the emission and discharges of priority substances should be prevented; the emission of priority hazardous substances are expected to be stopped completely by 2025. EQSs for priority and hazardous priority substances are set at an EU level under WFD and apply across all the member states. Nickel and lead are among the priority substances while cadmium is a priority hazardous substance. The specific pollutants are substances that are harmful to aquatic organisms and are discharged in large quantities. In the UK, copper and zinc have been identified as specific pollutants (Peter *et al.,* 2009). Lastly, the physico-chemical pollutants include temperature, dissolved oxygen and pH (UKTAG, 2008b). The AA- EQS and MAC-EQS of the selected heavy metals are shown (Table 2.4)

Table 2.4 The annual average and maximum allowable concentration of selected heavy metals dissolved in water

Heavy metals	Hazard classification	Annual average EQS in inland surface water (µg/L)	Maximum allowable concentration EQS in inland surface water (µg/L)
Cadmium	Priority hazardous substance	≤ 0.08 – 0.25 (depending on water hardness)	≤ 0.45 – 1.5
Lead	Priority substance	7.2	7.2
Nickel	Priority substance	20	20
Copper	Specific pollutant	1-28	NS[a]
Zinc	Specific pollutant	8-125	NS[a]

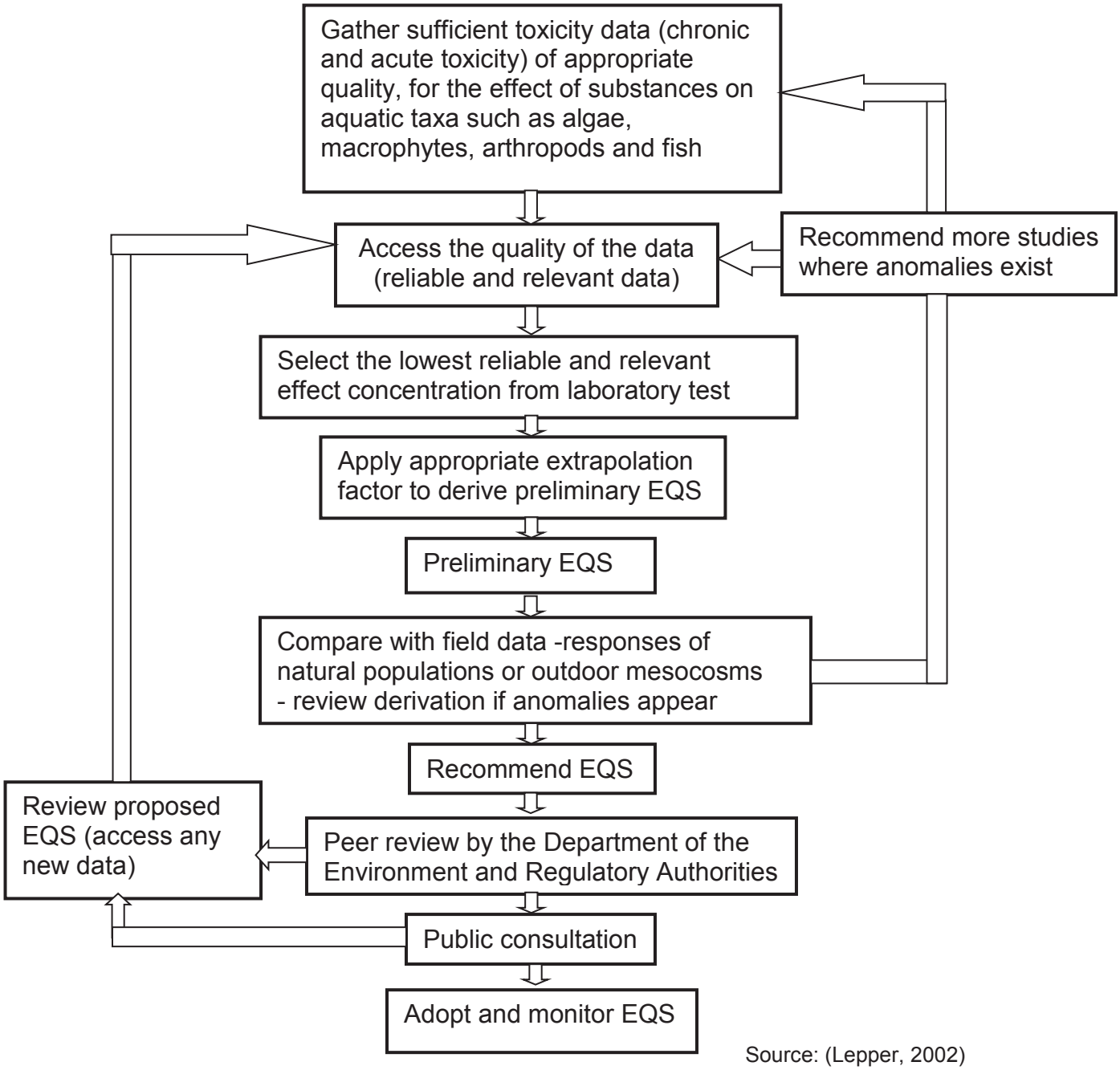
a - not set Source: UK Technical Advisory Group, 2008a

2.7.1 How EQS are derived in the UK

Establishing EQSs for substances in the environment is based on risk assessments and an estimate of 'safe' exposure levels with a considerable safety or assessment factor built in. The safety /assessment factor is intended to predict a concentration above which an unacceptable effect is most likely to occur. It is a precautionary measure that provides a wide safety margin in order to ensure protection of the environment. The size of the safety factor relates to the level of uncertainty in the data, and this factor ranges from 1-1000 depending on the available toxicity data (European Commission, 2003a).

Before EQS are derived, the substances such as the priority substances or specific pollutants for which standards are to be developed are first identified. Following the identification of such substances, risk assessment and toxicology data are collated for substances with available matched biological data on toxicity. Where sufficient data are available a standard is established, based on the biological toxicity data, which is used in water quality compliance monitoring. For substances such as specific pollutants with limited toxicity data, EQS derivation is based mainly on laboratory toxicity studies (UKTAG, 2008a). The collated laboratory toxicity data provides reliable and relevant data on the effects of substances on aquatic taxa, which are used to derive the predicted no effect concentrations of a substance for

different biota before applying an extrapolation factor (and thence a safety margin) to derive preliminary EQSs. The preliminary laboratory EQS is compared with field data (the responses of aquatic organism) on the effect of the substances in the natural aquatic ecosystem (Figure 2.3). The adopted EQSs are subject to peer review and public consultation before being adopted.



Source: (Lepper, 2002)

Figure 2.3 Derivation of environmental quality standards for sediment

2.7.2 Sediment quality guidelines

Sediment quality guidelines are used as indicators of water quality and as benchmarks for monitoring the quality of freshwater and marine sediment. There remains, however, no sediment EQS for metals or other priority pollutants at present in the UK (Hudson-Edwards *et al.,* 2008), compared to other European countries such as The Netherlands, Italy and France The challenge of developing uniform sediment environmental quality standards (SEQS) has attracted significant interest in recent years (Macdonald *et al.,* 2000; Wenning and Ingersoll, 2002; Kwok *et al.,* 2013).

The development of sediment quality guidelines is based around three main approaches namely:

(1) Effect based guidelines - This guideline is based on the effects or weight-of-evidence database from laboratory or field exposures of benthic organisms to contaminated sediments. They include spiked-sediment toxicity (Long *et al.* 1995), apparent effects threshold (Barrick *et al.* 1988), sediment quality triad (Chapman, 1996), screening-level concentrations (Persaud *et al.* 1993) and effect range approach (Long *et al.* 1998). A brief description is given below (Table 2.5).

Table 2.5 Effect based concentration approach to sediment quality guideline

Effect based concentration approaches	Description	Reference
Spiked-sediment toxicity approach	This approach is based on data generated from the response of benthic organisms to spiked sediment of known concentration.	Long *et al.,* 1995
Apparent effects threshold approach	It is usually based on the relationship between the measured concentrations of pollutants to observed biological effect. It is usually measured on dried weight of the pollutant.	Barrick *et al.*, 1988
Sediment quality triad approach	The sediment quality triad approach involves the use of sediment chemistry, sediment toxicity and benthic community to assess the degree of sediment contamination.	Chapman *et al*., 1999
Screening-level concentrations approach	This approach involves the matching of biological and chemical data collected in field studies to a specific benthic organism.	Persaud *et al.,* 1993
Effect range approach	The Effect ranges approach involves the use of large databases containing biological responses to sediment contaminants using other approaches to sediment quality guidelines. The data obtained are sorted into percentiles, the 10th percentile data is used as the Effects Range-Low (ERL), and the median as Effects Range-Median (ERM).	Long *et al.,* 1998

(2) Equilibrium based guideline (Equilibrium partitioning approach) - This applies existing water quality standards to sediment pore waters concentration (Di Toro *et al.* 1990; NOAA 1999). However, this approach does not account for sediment ingestion by organisms as a possible route of exposure since it does not include and surface bound contaminant.

(3) Background levels in the affected region - This is an old approach to sediment guidelines and involves the comparison of the bulk concentration of different contaminants in sediment with the background concentrations (Burton, 2002). The major disadvantage with this technique is that it does not give information about the ecological impact of contaminants on aquatic or benthic organisms due to absence of sediment chemistry information or laboratory toxicity test on aquatic

organisms (Burton, 2002). Two key guidelines are often used, the threshold effect sediment guidelines (concentration below which no adverse effect on sediment dwelling organisms are expected to occur) (Table 2.6) and the extreme effect sediment quality guidelines (concentrations above which adverse effects on sediment dwelling organisms are expected to occur) (Table 2.7) (Burton, 2002; MacDonald *et al*. 2000).

Prior to the development of the draft sediment quality guidelines (SQG) in the UK, sediment data were often compared with guidelines from other countries such as Canada, United States, the Netherlands, Australia and New Zealand. There is a huge difference in the SQG value for different countries, for example the threshold effect concentration of Zn ranged from 80mgkg^{-1} at Illinois to 400mgkg^{-1} in Venice Lagoon (Table 2.6). These SQG values can also differ with location in the United States of America, where different states have different SQG value (Table 2.6 and 2.7). These differences in SQGs are mainly due to the different geographical locations and different sediment characteristics, and it is now widely accepted that SQGs cannot be universal (Bjørgesæter and Gray, 2008; Simpson *et al.,* 2011). Even, in the European Community, member states are asked to develop suitable quality standards that apply to their environment. The variation in the SQGs value prompt the development of the Consensus based SQGs (MacDonald *et al.,* 2000). The consensus based SQG was developed to provide a unifying SQGs of the existing SQGs for the protection of benthic organisms in the United States and Canada (Table 2.6 and 2.7).

Table 2.6 Threshold effect sediment quality guidelines for selected heavy metals (mg kg^{-1})

Sediment Quality Guidelines	Cd	Cu	Pb	Ni	Zn	Reference
UK Draft sediment quality Threshold effect level **(TEL)**	0.6	35.7	35	18	123	Hudson-Edwards *et al*., 2008
Threshold effect level Florida, Canada **(TEL)**	0.6	35.7	35	18	123	MacDonald *et al.,* 2000
Effects range low (Ontario) **(ERL)**	5	70	35	30	120	MacDonald *et al.,* 2000
Lowest effect level (Florida) **(LEL)**	0.6	16	31	16	120	MacDonald *et al.,* 2000
Minimal effect threshold **(MET)**	0.9	28	42	35	150	MacDonald *et al.,* 2000
Consensus based -Threshold effect concentration (**CB TEC)**	0.99	31.6	35.8	22.7	121	MacDonald *et al.,* 2000
Environment Canada- Threshold effect level **(EC-TEL)**	0.68	18.7	30.2	15.9	124	Smith *et al.,* 1996
National Oceanic and Atmospheric Administration Effects range low (**NOAA ERL**)	1.2	34	46.7	20.9	150	NOAA[1] 1999
Australian and New Zealand Environment and Conservation Council Effects Range Low **(ANZECC ERL)**	1.2	34	47	21	200	ANZECC[2] 1997
Australian and New Zealand Environment and Conservation Council, Interim Sediment Quality Guidelines (**ANZECC ISQG-low**)	1.5	65	50	21	200	ANZECC[2] 1997
Sediment Quality Advisory Value, Threshold effect level **SQAV TEL)**	0.58	28	37	20	98	Swartz 1999
Sediment Quality Objective Netherlands Target **(SQO)**	0.8	36	85	35	140	ANZECC[2] 1997, Babut *et al.,*2003
Interim Sediment Quality Guidelines **Hong Kong ISQG-low**	1.5	65	75	40	200	ANZECC[2] 1997
low Interim Sediment Quality Value **(Hong Kong ISQV)**	1.5	65	75	40	200	Chapman *et al.,* 1999
Reference Value **(Flanders RV)**	1	20	0.1	28	168	De Cooman *et al.,* 1999
Slightly Elevated Stream Sediments (Illinois)	0.5	38	28	-	80	Burton, 2002
Limit class A (Venice Lagoon)	1	40	45	45	200	Apitz *et al.,* 2007
Limit class B (Venice Lagoon)	5	50	50	50	400	Apitz *et al.,* 2007

Source: Burton, 2002; De Deckere *et al*., 2011

1. National Oceanic And Atmospheric Administration (NOAA)
2 - Australian And New Zealand Environment And Conservation Council (ANZECC)

Table 2.7 Extreme effect sediment quality guidelines for selected heavy metals (mg kg^{-1})

Sediment Quality Guidelines	Cd	Cu	Pb	Ni	Zn	Reference
UK Draft sediment quality Predicted Effect Level (**PEL)**	3.53	197	91.3	35.9	315	Hudson-Edwards *et al.,* 2008
Toxic effect threshold **(TET)** Canada	3	86	170	61	540	MacDonald *et al.,* 2000
Severe effect level (**SEL)** Ontario)	10	110	250	75	820	MacDonald *et al.,* 2000
Consensus based probable effect concentration (**CB PEC)**	4.98	149	128	48.6	459	MacDonald *et al.,* 2000
SQG Netherland Intervention	12	190	530	-	720	ANZECC 1997
Reference Value **(RV)** Flanders	6	126	0.8	174	1057	De Cooman et al. 1999
Extreme Elevated Stream Sediments (Illinois)	20	200	100	-	300	Burton, 2002
Australian and New Zealand Environment and Conservation Council (**ANZECC)**	10	270	220	52	410	Long *et al.,* 1995

(Source: Burton, 2002 ; McCready *et al.,* 2006)

2.8 River sediment sampling

There is a need for better sampling and monitoring techniques for sediment, especially with respect to establishing and achieving sediment quality guidelines (Taylor and Owens, 2009). One of the challenges for setting sediment quality standards has been linked to the lack of standardization in sediment sampling techniques (Crane, 2003). An effective, practicable and reproducible method of sediment sampling will be an important tool in developing sediment environment quality standard. A good sampling method should be able to collect samples that are representative of the variability in heavy metal concentrations at the sampling site and should be able to provide sufficient sample for analytical purposes (Simpson *et al.,* 2005). This research compares different sampling techniques used in collecting sediment from the bed, bank and suspended sediments of an urban river, and seeks to identify the most suitable sediment compartment to sample. The bed sediment is commonly used as a basis for monitoring heavy metal concentrations in sediment and has been used in setting sediment quality guidelines (SQG)/ sediment quality standards (SQS) in most countries such as Canada, Australia, Italy and the Netherlands (Burton, 2002). The draft UK sediment quality guidelines are likely to be based on bed sediment (Hudson-Edwards *et al.,* 2008). The Fraunhofer Institute

(2002) suggested that suspended sediment should be measured and compared with environmental quality standards rather than bed or bank sediment because suspended sediment retains and transports recent contaminants (Crane, 2003). However, suspended sediments tend to show more physical and chemical variability compared to bed sediment, and the quantity of suspended sediment collected does not always meet the mass requirement for chemical and physical analysis (Horowitz 1991).

Sediment sampling should also take into consideration natural processes such as rainfall, topography and morphology because these are likely to affect the rate at which sediment is transported, remobilised and deposited in river systems (Horowitz, 1991). A knowledge and understanding of these variations in river characteristics and sediment properties form an important aspect of an effective sediment sampling programme. Some of the challenges for aquatic sediment sampling include:

(1) Complex nature of sediment particles: Sediment consists of a highly variable mixture of particles of different sizes, and mineral and organic matter composition which determines the sediment characteristics (Allen, 1965; Droppo, 2001; Ongley and Bynoe, 1982). A sampling technique that ensues samples are representative of the sediment environment is vital, and should form part of the sampling objective (Simpson *et al.,* 2005).

(2) Changes in environmental conditions*:* Another factor that should be considered when sampling sediment is changing environmental conditions such as pH and redox potential overlying water. Variations in the rate at which sediment is transported as a result of fluctuations in weather conditions such as rainfall also are important (Woodruff *et al.,* 2001; Walling and Fang, 2003). The physico-chemical characteristics (pH, temperature and dissolved oxygen) of the river should be measured at different points within the river during sample collection at these points.

(3) Storm and flooding events: The majority of heavy metal contaminated sediments are transported during periods of heavy rainfall (Komar, 1988; Foster *et al.,* 2000; Zonta *et al.,* 2005). There is clearly a need to collect sediment samples

(suspended, bed and bank sediment) after every storm event in order to monitor the potential variations in the concentration of heavy metal contaminants resulting from storm events.

(4) River flow rate: The flow rate and sedimentation rate of most rivers differs from one section of the river to the other which could be due to geomorphological settings and may affect the rate of sediment deposition (Adame *et al.,* 2010), and aquatic organisms activity (Richey *et al*. 1986; Taylor and Cooke, 2012). Sediment samples should be collected from different locations in a river to account for this variability and flow rate should, ideally, be determined.

(5) Frequency of sampling: The variability in sediment characteristics, especially suspended sediments, as a result of changing environmental conditions should be assessed by frequent sampling, especially before and after heavy storm events. However, where the rate of sedimentation is low, sufficient time should be allowed to collect sediment samples (Simpson *et al.,* 2005); particularly in methods that provide time integrated suspended sediment samples. A set sediment sampling programme needs to be followed in order to accurately assess the total particulate flux and variability of heavy metal concentration in sediment.

Some of the commonly used methods for sampling river sediment are grab samplers, a hand trowel for the bed and bank sediment (Mudroch and Azcue, 1995; Simpson *et al*., 2005; Blanchard *et al.,* 2010), and the time integrated tube sampler for suspended sediment (Philips *et al*., 2000).

Chapter 3

Study Area and Sampling Location

3.0 Introduction

This research was focused on sampling an urban river in London where anthropogenic activities are expected to make a significant contribution to the concentration of the selected heavy metals in sediment (Environment Agency, 2011b). A number of rivers were considered as sampling sites with respect to their physical characteristics, accessibility and distance to the laboratory. The River Lee, a major tributary of River Thames in East London, was initially examined for its suitability as a sampling site. However, various modification works have altered the natural properties (flow processes and support for aquatic life) extensively, making this river system inappropriate for this study. The Ravensbourne River in the South East of London was then examined for its suitability and subsequently chosen as the sampling site. It was selected because of the ease of accessibility and location in the highly urbanised area of South East London, surrounded by Lewisham, Bromley and Catford. This chapter describes the Ravensbourne catchment - geomorphology, geology, hydrology, historical and current industrial activities along the river, water quality and the commonly found biological species in the Ravensbourne River. Finally, the sampling design and plan with respect to the research aim and objectives is described.

3.1 History of the Ravensbourne River

The story behind the history of the Ravensbourne River dates back to 55BC, at the time Julius Ceasar and his army camped at Keston during an invasion of Britain. A raven was constantly spotted near the camp of Ceasar and his troop. The raven's visit was eventually discovered to be as a result of a spring named after the Raven (Ravensbourne River) (Mackay, 1840; Knight, 1842). The Ravensbourne rises as a chalk spring at Keston. The spring is regarded as a holy well because it was believed to possess healing properties, and has been reportedly used for medicinal purposes (Knight, 1842). Other holy wells such as the Ladywell (a holy well dedicated to the Virgin Mary) have been associated with the River Ravensbourne (Sutherland, 1915).

3.2 Ravensbourne Catchments

The Ravensbourne River is a tributary of the River Thames located in a heavily built-up area of South East London (Figure 3.1). It rises as a Chalk spring in Caesar's Well at Keston, and flows through the London Boroughs of Bromley, Greenwich and Lewisham before joining the Thames at Deptford (Knight, 1842; Lewisham Council and Environment Agency, 2010). The Ravensbourne is 17.4km long and covers a catchment area of 180km^2. The major tributaries that feed into the Ravensbourne are the Pool River which joins the Ravensbourne at Catford, and the River Quaggy, joining the Ravensbourne at Lewisham (Figure 3.1).The Chaffinch Brook and River Beck are tributaries of the Pool River. The Pool River and the South branch of the Ravensbourne rises between Addington and West Wickham.

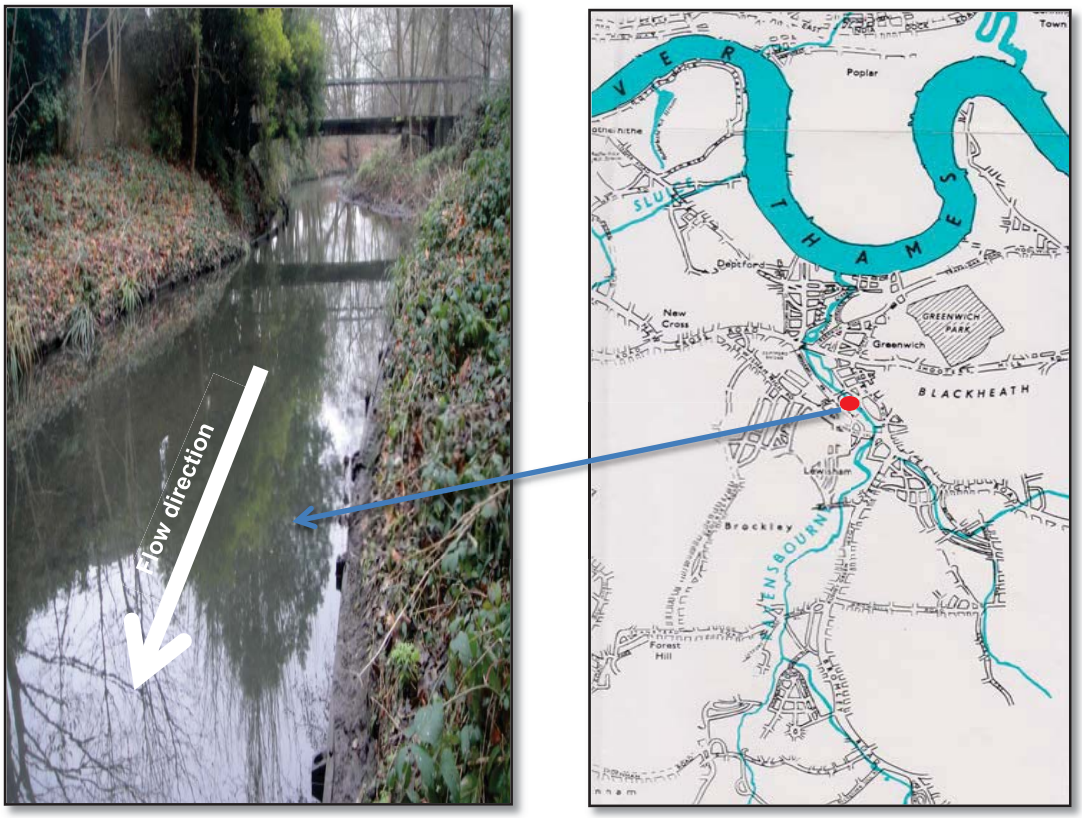
(Source: The River Restoration Centre, 2011)

Figure 3.1 Ravensbourne River Catchment (dark shading) within Greater London

3.3 Sampling Location

Sediment samples were collected from the Ravensbourne River in Ladywell Field, TQ 3776874618 (51.453793N, -0.0186038), (Figure 3.2) 19m above sea level from July, 2010 to December 2011. Storm samples were collected in February 2011 and May 2012. This section of the Ravensbourne River in Ladywell was chosen for study because of accessibility and proximity to transportation. The sampling location is about 150m from Ladywell rail station to the east, about 500m from a minor road, approximately 2.5km to Catford rail station and the major A205 South circular road, which is north of the sampling location.

The river bed at the sampling location consists mainly of gravel (>2mm) material, and the bank is made of fine materials, predominantly sand sized materials. The river depth (0.2m - 0.5m) and discharge (83 Ls^{-1} – 2,370 Ls^{-1}) varied across the sampling location (Appendix 2). In the sampling location, the river was often slightly deeper near the left bank (facing downstream) and the river velocity was always measured as being faster near the left bank of the River compared to that near the right bank **(**Appendix 2**).** Close to the right bank of the sampling area was a concrete fenced wall of the Lewisham Hospital, and the left bank led to Ladywell Fields.



(Source: Barton, 1992)

Figure 3.2 The sampling location on the Ravensbourne at Ladywell field

Ladywell Fields is about 1.61km long and located between Catford and Ladywell (Lewisham Council, 2013). It consists of small parks, a children's playground, café, leisure centre and sports facilities such as tennis court and football pitch (Lewisham Council and Environment Agency, 2010). A meandering V-shaped channel, backwater and footbridge cuts across the middle section of Ladywell Fields (River Restoration Centre, 2008). Ladywell station is located east of the sampling location, and Catford rail station is location north of the sampling location. Lewisham town centre are located further east of the sampling location, and the sampling site is located about 200m from major roads. The Ravensbourne at Ladywell is surrounded by stands of scrub, grasslands and tall herbaceous vegetation (Baxter, 2011). The commonly reported aquatic organisms sighted upstream of the sampling location are kingfishers, eels, moorhens and sticklebacks (Lewisham Council and Environment Agency, 2010). Oligochaetes and shrimps were commonly sighted in the Ravensbourne at Ladywell during the monthly sample collection for this study. The

Ravensbourne at Ladywell has a low monthly discharge as shown by measurements taken during this study except during the February 2011.

In the Ladywell section of the Ravensbourne catchment, road dust, channel erosion and cultivated topsoil are likely to be the main sources of sediment. This is mainly due to the proximity of the sampling location to major roads; the creation of a secondary channel and back water in the middle of Ladywell Fields, grass mowing with a tractor and the cultivation of plants near the sampling location. The detailed results of the physical characteristic of the Ravensbourne during sampling are presented in the results section (Section 2 of this study).

3.4 Industrial development and activities along the Ravensbourne River

The existence of the Ravensbourne River attracted human beings to its catchments in very early times (Duncan, 1963; Coulter, 1999). This human attraction led to the development and industrial activities that occurred within the Ravensbourne River. The rapid development of the Ravensbourne catchment was mainly due to several urban regeneration projects such as the construction of railway stations, building of houses and an increase in population (Lewisham Council and Environment Agency, 2010). During the early 18th century, Kent Water Works used the Ravensbourne River as a source of domestic water supply for the inhabitants of Deptford, Greenwich, Surrey and Kent (Knight, 1842). There was a cholera outbreak at Deptford in 1954 due to the contamination of the iron Kent water pipes from sewage discharge on the ground (Dickinson, 1954). A major flooding event occurred between Lewisham and Beckenham in September 1968 following a week of heavy rainfall (Barton, 1992). A flood storage area with up to 85,000m^3 capacity was constructed within the Ravensbourne Catchment in 2007 as a result, in a flood defence scheme. A severe sewage problem was reported in Deptford in the mid -18th century (Lewisham Council and Environment Agency, 2010), and a sewer was built near Bell Green to deal with the severe sewage problem (Lewisham Council and Environment Agency, 2010).

Historical records of industrial activities on the Ravensbourne River show the river was used as source of energy for milling machines, eleven mills were recorded on

the Ravensbourne in the eleventh century (Barton, 1992; Talling, 2011). Other industrial activities included cutlery factories, gasworks, breweries, chemical works, and ship building industries in the 16th century. A power station was also located at Deptford (PortCities, 2011), and the manufacturing of copper sulphate ($CuSO_4$) took place in the 19th century (Environment Agency and Lewisham Council, 2010). Other industrial activities recorded but without dates along the Ravensbourne River are the Artisan corn Mill, Ford Mill, Grange Mill and Catford Bridge Mill located at the confluence of the Ravensbourne and Pool River (Collins, 2010).

Most of these historical industrial sites are located downstream of the sampling location and will not have any impact on the sampling location. They are, however, indicative of the industrial heritage of the area. Some of the past industrial activities located upstream of the sampling location are the water mill in Catford which could be a possible source of zinc from the wheels of the machine if made of galvanised metal, the glass mill in Bromley which could be a possible source of lead, the cutlery industry in Beckenham which could be a possible source of copper and nickel, and the Fox Electroplating industries in Sydenham (Table 3.1). The Fox-plating company offer electroplating services with nickel, zinc and copper among other metals capable of causing river pollution from effluent discharge. Fox plating was prosecuted in April 2007 for discharging waste water containing cyanide and heavy metals in the Ravensbourne River (CIEH, 2008; Environment Agency, 2011a). Some on-going industrial activities located upstream of the sampling location includes the Churchfields Transfer Station, a waste (including construction waste) recycling centre located at Beckenham (about 7km from sampling location), and the London Recycling Centre located in Sydenham (about 6km from sampling location) which recycles diverse types of waste. Both these are used mainly as Transfer Stations for household, commercial and industrial waste. The third industrial activity is the Sydenham Scrap Metal Recycling site (about 6km from sampling location) (Table 3.1).

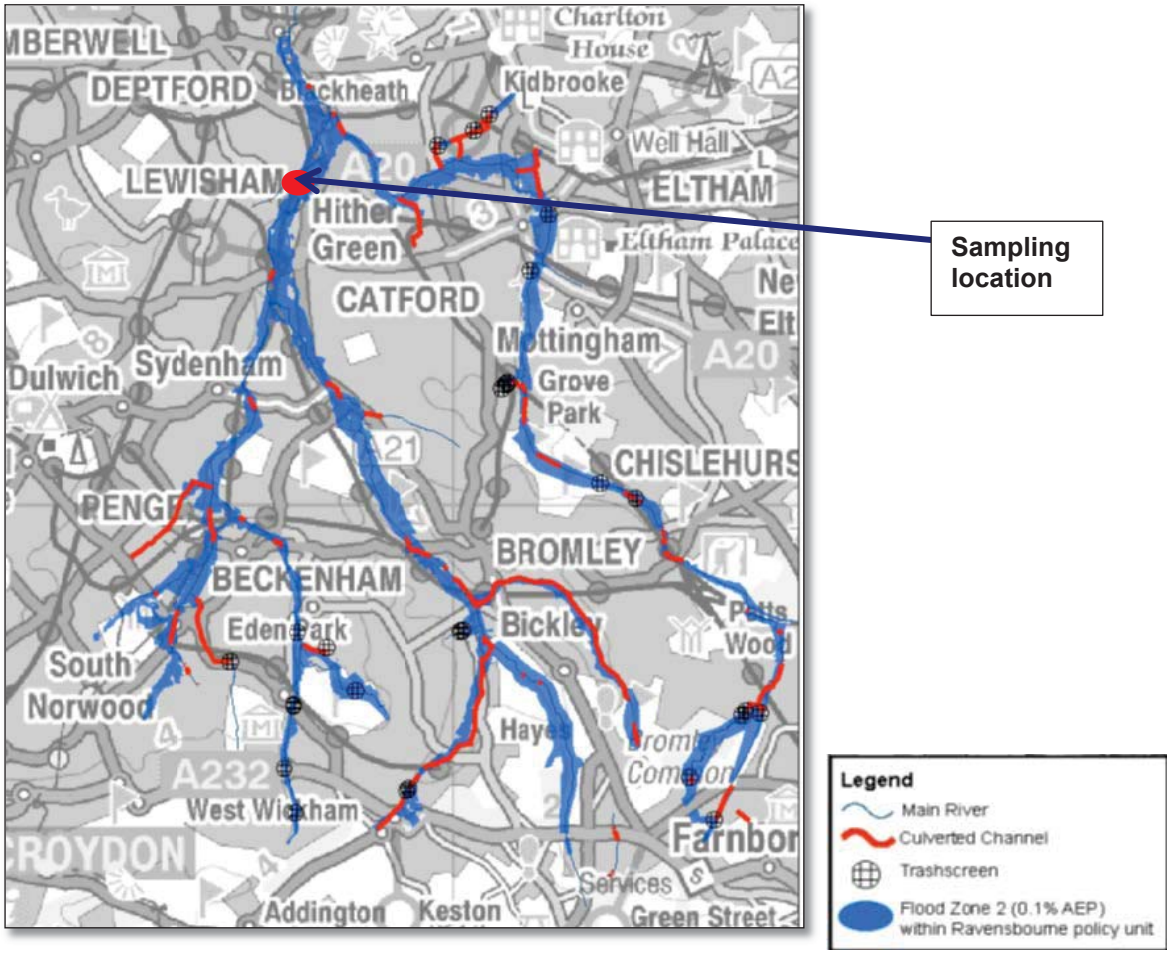
Table 3.1 Historical Pollution in the Ravensbourne River Catchment

Activity	Date	Person/Company responsible	Present location	Source
Water Mill	14th century	Knapp's family	Knappmill, Catford (about 2.5 km upstream of sampling site)	Collins, 2010
Manufacturing of high quality cutlery	1789	Ephraim and John How	The lower mill - the mill pond, Southend (about 4.5km upstream of sampling site)	Barton, 1992; Spurgeon,1999
Electroplating	April, 2007	Stephen Fox, owner of Fox-plating.	Rutland Park, Lower Sydenham (about 6km upstream of sampling site)	Chartered Institute of Environmental Health. 2008
Glass Mill	N/A	N/A	Bromley (about 11.6km upstream of sampling site)	English, 1992

N/A- Not available

3.5 Geomorphology of the Ravensbourne River

The Ravensbourne River and its tributaries are one of the most culverted rivers in London flowing across densely populated areas such as Lewisham and Catford (Barton, 1992; Copas, 1997). In a reflection of many urban rivers more than 50% of the Ravensbourne catchment is heavily modified both by flood defence structures, and to cope with rising population (Lewisham council and Environment Agency, 2010). In the past, most parts of the Ravensbourne were either buried underground, culverted behind railings or covered by vegetation (Figure 3.3) (River Restoration Centre, 2008). The culverted areas and flood zones of the Ravensbourne catchment are shown below (Figure 3.3).



Source: London Borough of Bromley, 2013

Figure 3.3 The Culverted channels and flood zone of the Ravensbourne Catchment

Over the last 22 years, the river has benefitted from regeneration projects carried out by the River Restoration Centre (Lewisham Council and Environment Agency, 2010). Various modification works have been carried out along different sections of the river to restore it to a natural state and to increase the general quality of life for local residents. The major modifications and restoration works on the Ravensbourne began in 1991 (Table 3.3). Some parts of the river such as at Southend, Lewisham and Deptford Bridge were, until recently, filled with waste materials such as household waste, shopping trolleys and dead plant materials that have obstructed the natural flow of the river (Collins, 2010). These obstructions have been cleared and natural river flow re-established in these locations after the river restoration project.

Table 3.2 River Restoration projects carried out on different parts of the Ravensbourne River

River name	Location	Date of completion	Main reason
Beck	Beckenham	1991	Development of habitat and landscape
Ravensbourne East branch	Bromley Common	1993	Development of habitat and landscape
Ravensbourne	Norman Park, Bromley	2000	De-culverting and flood risk management
Spring Brook	Shaftesbury Park, Downham	2000	Community demand, habitat and landscape
Ravensbourne	Hayes	2006	Fisheries
Ravensbourne	Ladywell Fields	2008	Enhance river corridors, landscape and habitat improvement.
Ravensbourne	Bell Green	2011	Fisheries

(Source: The River Restoration Centre, 2011)

The Ravensbourne at Ladywell Fields was modified by the Quality Urban Environments for River Corridor Users and Stakeholders (QUERUS), funded by the London Borough of Lewisham, in partnership with Chester City Council and EU's LIFE Environment Programme. The project enhanced the Ravensbourne corridor by creating a channel that meanders through the fields (River Restoration Centre, 2008). The river was also widened and the banks were protected with toe-boards. In addition to various regeneration projects by the River Restoration Centre along the Ravensbourne, river clean-up projects have also been carried out since 2012 by volunteers from the Thames21 group to remove invasive plant species (Himalayan balsam) and pick up litter (Hall and Coode, 2011).

3.6 Geology of the Ravensbourne

The Ravensbourne drains parts of the South London clays, gravels and stony sands as it flows towards the River Thames, and the lower catchments are mainly

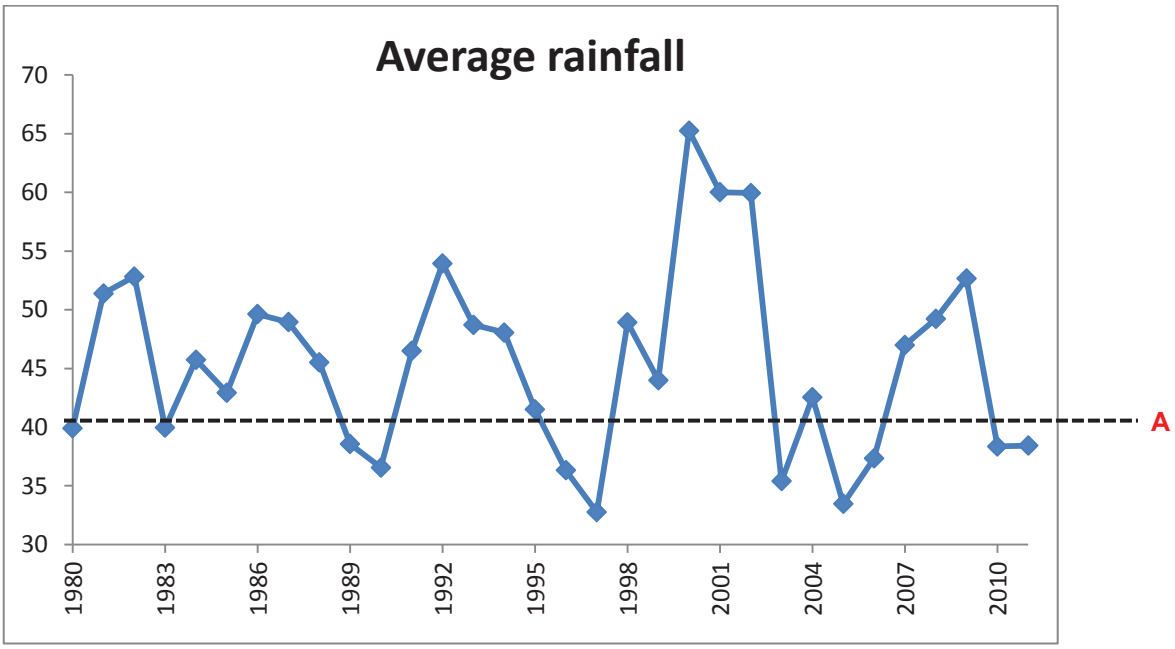
composed of impervious Eocene deposits (Baxter, 2011). The geology and topography of the upper rivers consist of the Chalk Slopes of the North Downs (Baxter, 2011). The bedrock geology of the sampling area is made of the Lambeth Group-clay, silt and sand and gravel, and the superficial deposits consist of alluvium – clay, silt, sand and gravel (Baxter, 2011).

3.7 Hydrology of Ravensbourne River

The Thames catchment has been described as one of the driest catchments in the UK (Environment Agency, 2004b). The Ravensbourne catchment, like most UK catchments, has experienced considerable variations in weather conditions in recent years. The Meteorological Office has reported warmer winters and wetter summers in recent years for the UK (Lewisham Council and the Environment Agency, 2010). It is well established that variations in weather conditions such as rainfall significantly affects river and ground water levels (Jan *et al*. 2007) and the Ravensbourne will be affected in a similar way.

The Ravensbourne River serves as a source of water supply for domestic, agricultural and industrial purposes, and in the energy sector (Environment Agency, 2011a; 2011b and 2011c). There are over 15 licensed abstractions in the Ravensbourne catchment, 8 in the Bromley Borough, 7 in the Lewisham Borough and 16 in the Greenwich borough including other rivers such as the Marsh Dykes and Shuttle River that forms part of the Greenwich borough (Environment Agency, 2011c). Over 90% of the abstractions from the Ravensbourne River are taken from ground water in the confined Chalk aquifer (Environment Agency, 2011a and 2011b).

During periods of high temperature and low rainfall, river velocity is at a minimum and the concentration of contaminants is usually high in the water column due to low levels of dilution (Dickinson, 1954).The year 2011 was reported as the second warmest year since 1910, after 2006 (Meteorological Office, 2012), and contaminant levels would be expected to be higher in the water column. The graph below (Figure 3.4) shows the annual average rainfall at Crossness, South East London which is about 10miles from the sampling location.



(Source: Meteorological Office, Personal communication 2012)

A = 43.84mm and indicates average rainfall during the sampling period (Sept. 2010-Dec.2011)

Figure 3.4 The annual average rainfall (mm) at Crossness, South East London from 1980-2011

3.8 Water Quality of the Ravensbourne River

The Environment Agency (2013a) recorded some water pollution incidents that have occurred in the Ravensbourne Catchment, upstream of the sampling location. Most of the pollution incidences occurred at Bromley, with one of these, in 2005, a major organic pollution incident (Table 3.3).

Table 3.3 Pollution incidences reported within the Ravensbourne catchment

Local Authority	Date	Environmental impact	Incident number	Impact to water	Pollutant	Location
Bromley	28-Aug-01	Significant	41394	No Impact	Inert materials	Elmers End
Bromley	05-Nov-02	Significant	118911	Significant	Inert materials and waste	Beckenham
Bromley	03-Mar-03	Significant	140589	Minor	Sewage materials	Elmers End
Bromley	11-Feb-03	Significant	136229	Minor	Sewage materials	Elmers End
Bromley	22-Apr-03	Significant	153045	Minor	Sewage materials	Elmers End
Bromley	15-Jun-05	Major	320613	Major	Organic chemicals/products	New Beckenham
Bromley	09-Jun-09	Significant	686276	Significant	Oils and fuel	New Beckenham
Bromley	13-Jun-10	Significant	789729	Significant	Sewage materials	Bromley Common
Bromley	13-Jun-10	Significant	789729	Significant	Other pollutant	Bromley Common
Bromley	21-Jan-12	Significant	956105	No Impact	Other pollutant	New Beckenham
Bromley	30-Jan-12	Significant	958151	No Impact	Other pollutant	Lower Sydenham

(Source: Environment Agency, 2013a)

The details of the inert materials were not provided by the Environment Agency but inert materials are generally not chemically reactive. The pollution incidents closest to the sampling location were the two that occurred at Sydenham contributing significant inorganic pollution to the Ravensbourne River. The details of the inorganic pollutants were not stated but they are believed to be related to metals, and are probably the same pollution incident reported in April 2007 by the Chartered Institute of Environmental Health (CIEH) (Table 3.1).

The Water Framework Directive (2000) requires the quality of water bodies based on their ecological status, chemical and biological status to be determined and monitored. Overall, the ecological status of the Ravensbourne river at the sampling location (between Catford and Deptford) is poor river quality (Table 3.4a), and it is predicted not to achieve a good status by 2015 (Environment Agency, 2011a, a, c). The chemical status usually includes the test for priority substances such as organic pollutants and metals as defined by the Water Framework Directive (Table 3.4b). The sampling location has a poor biological status for most of the test organisms

(Table 3.4c), and the aquatic habitat is limited to pollution tolerant species such as crayfish and aquatic worms (Environment Agency, 2011a).

Table 3.4(a) Ecological status (biological, physico-chemical and hydro-morphological status)

Water course	2009 Classification Status	2015 Prediction
Pool River	Moderate	Moderate
River Ravensbourne (Keston - Catford)	Poor	Poor
River Ravensbourne (Catford - Deptford)	**Poor**	**Poor**
Quaggy	Poor	Poor

(Source: Environment Agency, 2011a)

Table 3.4(b) Chemical water quality - physico-chemical status under the Water Framework Directive

Water course	Physico-Chemical status	Dissolved oxygen	pH	Phosphate	Ammonia
Pool River	Not assessed	-	-	-	-
River Ravensbourne (Keston - Catford)	Good	High	High	Good	High
River Ravensbourne (Catford - Deptford)	Moderate	High	Moderate	Poor	High
Quaggy	Not assessed	-	-	-	-

(Source: Environment Agency, 2011a)

Table 3.4(c) Biological status under the Water Framework Directive

Water course	Biological status	Diatoms	Macro-phytes	Macro-invertebrates	Fish
Pool River	Poor	-	-	Moderate	Poor
River Ravensbourne (Keston - Catford)	Poor	-	-	Moderate	Poor
River Ravensbourne (Catford - Deptford)	Poor	Poor	Moderate	Moderate	Poor
River Quaggy	Poor	-	-	Poor	Poor

(Source: Environment Agency, 2011a)

The major reasons for not achieving good ecological status in the Thames River Basin were physical modification due to urbanization, diffuse pollution from agriculture and mixed urban run-off, and from point source sewage treatment works (Environment Agency, 2009a).

Monitoring data obtained from the Environment Agency covers a 10 year sampling period (from 2000-2010) for Bromley (upstream of sampling location) and Ladywell monitoring (**Table 3.5**).

Table 3.5 The physical/chemical characteristics of the water column for the Ravensbourne River at Bromley and Ladywell (2000-2010)

Average reading	Bromley (2000-2010) (n=134)	Ladywell (2000-2010) (n=107)
pH	7.3 – 8.9	6.7 – 9.1
Temperature (^{0}C)	0.6- 22.4	4.0 – 22.4
Dissolved Oxygen (mg/l)	5.9 – 16.0	5.7 – 17.2
Ammonia (mg/l)	0 – 0.2	0.0 – 0.4
Nitrate (mg/l)	0.3 – 8.0	1.51 – 7.0
Chloride (mg/l)	16.0 - 49.4	16.8 – 155.0
Orthophosphate (mg/l)	0 – 1.1	0.1 – 0.7
Phosphorus (mg/l)	N/A	N/A
Magnesium (mg/l)	N/A	N/A
Calcium(mg/l)	N/A	N/A
BOD (mg/l)	0- 5.6	0.0 – 9.9
Cadmium (ppb)	N/A	N/A
Copper (ppb)	N/A	N/A
Nickel (ppb)	N/A	N/A
Lead(ppb)	N/A	N/A
Zinc (ppb)	N/A	N/A
Iron (ppb)	N/A	N/A

N/A- not available (Source: Environment Agency, personal communication) 02/11/2010)
mg/l - milligram per litre, ppb - part per billion

The monitoring data provided by the Environment Agency was incomplete for Bromley and Ladywell. This was particularly true of the concentration of heavy metals in the water column. There were no Environment Agency data for heavy metal concentrations in the water column for Bromley and Ladywell. The pH was slightly alkaline suggesting that heavy metals are likely to be associated mainly with sediment.

3.9 The background characteristics of soil and metal concentration in sediment around the sampling location

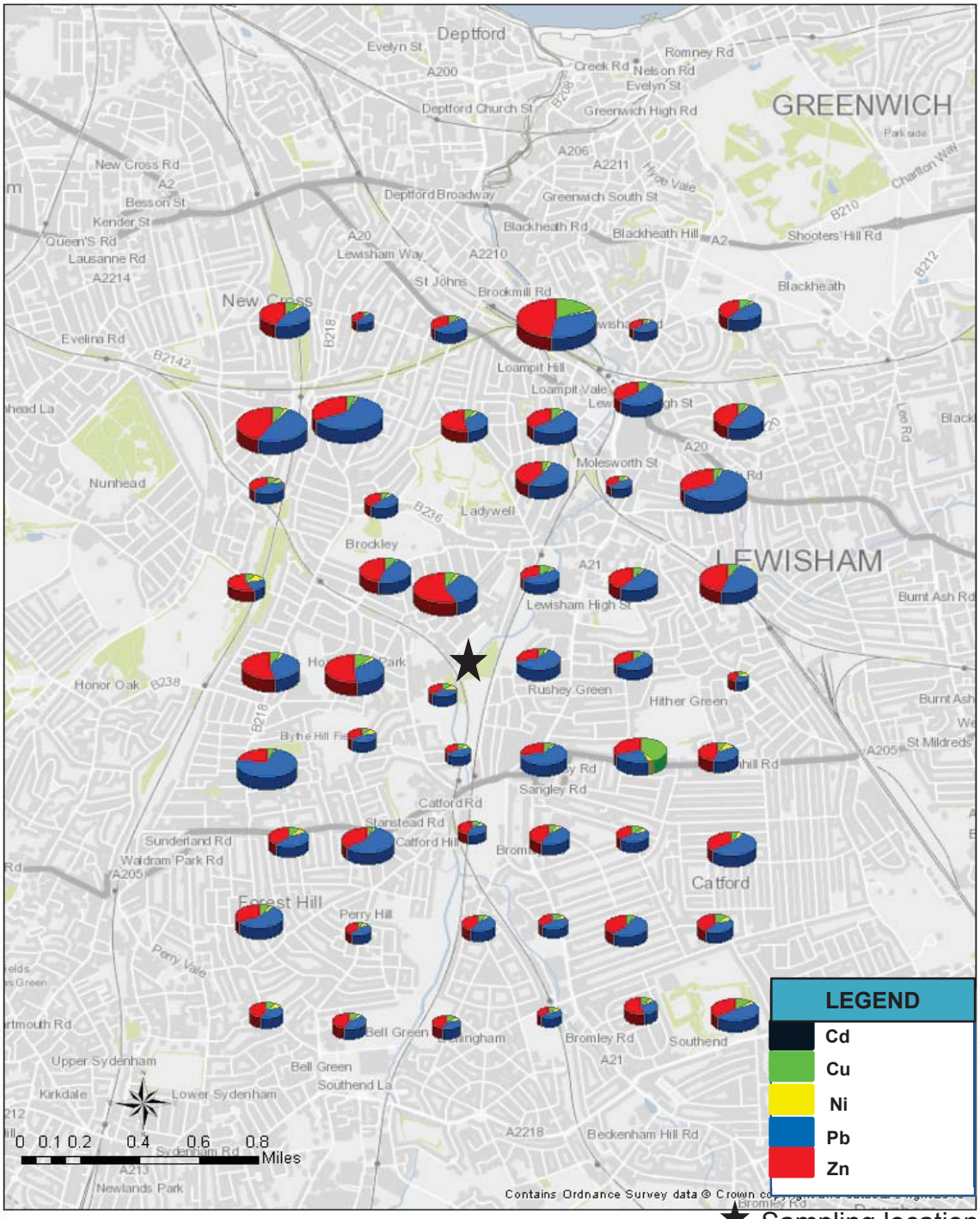
The British Geological Survey has no background heavy metal concentration for sediment in the research area. The background levels in soil of selected metals were investigated using the data provided by the British Geological Survey (BGS London Earth Project, personal communication, 10/12/2012). The BGS collected top soil (0-10cm) samples from the area covering Bromley (51.432353 - 0.004968165) to Lewisham (51.469009, -0.0386445362), and analysed all chemical elements by X-Ray Fluorescence Spectroscopy (XRFS).The concentration of selected heavy metals (Cd, Cu, Ni, Pb, and Zn) and other metals such as aluminium, iron and chromium that might also affect the soil mineralogy are also given (Table 3.6). The concentration of salts (K, Na, Ca, and Mg), the pH, and organic matter content by loss on ignition (LOI) are also listed.

Table 3.6 The background characteristics of soil between Bromley and Lewisham carried out in 2009 (n=53)

Parameter	Range values
pH	4.72 - 7.32
LOI (%)	4.5 - 13
Calcium (mg/kg)	5,818 - 40,638
Magnesium(mg/kg)	2,412 – 15,681
Potassium(mg/kg)	6,226 – 21,168
Sodium(mg/kg)	1,484 – 5,511
Phosphorous(mg/kg)	786 – 4,539
Chromium (mg/kg)	43 -113
Aluminium (mg/kg)	22,747 – 81,466
Iron (mg/kg)	17,135– 45,262
Cadmium (mg/kg)	0.3 - 2.1
Copper (mg/kg)	20 - 510
Nickel (mg/kg)	14.5 - 61
Lead (mg/kg)	52– 1,346
Zinc (mg/kg)	81 – 1,280

(Source: BGS London Earth Project, personal communication 02/11/2010)

A GIS mapping for the concentration of selected heavy metals in soil based on the location and concentration of contaminant, using the data obtained from the British Geological Society is shown in Figure 3.5. Lead and zinc were the dominant heavy metals in soil, responsible for about 80% of the concentration of metals in total (Figure 3.5). The size of the pie chart in each soil background location varies with the total concentration of all heavy metals. Most of the higher concentrations for total metal load were located downstream of the sampling location (Figure 3.5).



★- Sampling location

Note: The diameters of the pie charts are proportional to the sum of the metal concentration

Figure 3.5 Location of the background concentration of elements around the Ravensbourne at Ladywell Fields (the study location).

3.10 Biological species commonly found in the Ravensbourne catchment

The urbanization and the poor water quality of the Ravensbourne River have led to loss of species diversity. The Ravensbourne aquatic habitat is limited to pollution tolerant species such as the non-native Turkish crayfish and aquatic worms (Environment Agency, 2011a). Common species found in the Ravensbourne River and its tributaries (particularly between Keston and Catford) are bullhead, stone loach, stickleback and minnow (Environment Agency, 2011a, b, c).

3.11 Sampling design and plan

Sediment and water sampling programmes were designed to address the research objectives of this study. The two most important objectives of this study were to measure concentrations of selected heavy metals in different sediment compartments (bed sediment, actively transported sediment and sediment deposited on the bank) and to establish the most reproducible and economical sampling method for these sediment compartments using the selected heavy metals (cadmium, copper, nickel, lead and zinc) as model pollutants.

3.12 Summary

The chapter describes the study area of this research which is focussed on the Ravensbourne River. It is among one of the most cultverted rivers in London, with poor water quality, low river velocity and various historical and recent industrial activities located along the river. However, various River Restoration projects have helped to restore some part of the river to a natural course, making it an ideal urban river to study sediment. The next chapter describes the field sampling methods for sediment and water collection, and the analytical techniques used in studying the physical and chemical characteristic of the river. The justification for each sampling and analytical techniques are also described.

Chapter 4

Materials and Methods

4.0 Introduction

This chapter describes the different sampling techniques used in collecting sediment and water samples from a section of the Ravensbourne River in Ladywell Fields. Sediment plays an important role in water quality, and the need for sediment monitoring in order to achieve the EU Water Framework Directive objectives has gained recognition in recent years. The most important objective of most sediment sampling is to collect representative samples and to maintain sample integrity (Simpson *et al.,* 2005). The sediment and water sampling programme was designed to fulfil the research objectives (Symader, 1992). The main objectives of this study were to compare the concentrations of Cd, Cu, Ni, Pb and Zn in both the water column and in the different sediment compartments (bed sediment, actively transported sediment and sediment deposited on the flood plain) and to establish the most reproducible and economical method for sampling river sediment. Different sampling techniques were applied in sampling the bed, bank and suspended sediment. Sediment and water samples were collected simultaneously to compare heavy metal concentration. A risk assessment was undertaken prior to the field work to determine the risk associated with sampling on the River Ravensbourne (appendix 1). Suitable precautions were taken and sediment samples were not collected during flood conditions (appendix 1). This chapter describes the sample collection and the laboratory analysis. The technique used for water collection and the techniques used to sample the bed, bank and suspended sediment in the Ravensbourne River are described. The laboratory analysis section provides details of the different analyses carried out on the water and sediment samples, ranging from sample preparation to the metal analysis technique, and examines the reasons for the choice of method where appropriate. A description of the statistical analysis and quality control is also described.

4.1 Sample Collection

Surface sediment (depth range of 0-10mm) is usually collected when sediment is monitored for quality purposes (Simpson *et al.,* 2005). A pre –sampling was carried out in July 2010 for the bed and bank sediment. Additional bed and bank surface

sediment samples were collected over a period of 12months (January 2011-December 2011) with some differences in the regime when sampling time falls over the weekend or samples could not be feasibly collected. The suspended sediment and water samples were collected from September 2010 to December 2011 (Table 4.1). Storm event samples were collected in February 2011 and May 2012. The samples were collected to be representative of different sediment compartments and the water column and, where possible, it was ensured that sufficient sample mass was collected for analytical purposes.

Table 4.1 The sampling regime for water and sediment samples at Ladywell Fields, River Ravensbourne

Sample collection date	Water[a]	Bed sediment[b]	Bank sediment	Suspended sediment[c]
13/07/2010	**x**	√	√	**x**
27/09/2010	√	**x**	**x**	**x**
27/10/2010	√	**x**	**x**	**x**
27/11/2010	√	**x**	**x**	**x**
30/11/2010	√	**x**	**x**	**x**
27/01/2010	√	√	√	√
26/02/2011	√	**x**	√	**x**
19/04/2011	√	√	√	√
27/05/2011	√	√	√	√
27/06/2011	√	√	√	√
27/07/2011	√	√	√	√
27/08/2011	√	√	√	√
27/09/2011	√	√	√	√
27/10/2011	√	√	√	√
26/11/2011	√	√	√	√
14/12/2011	√	√	√	√
05/05/2012	√	√	√	√

a Water column samples in triplicate **√- Sampled, x- Not sampled**
b a composite of a minimum of 4 samples
c Two sediment traps for each river bank

Most of the monthly collected suspended sediment and the <63µm bed sediment collected were not sufficient for all laboratory analysis as the sampling period was one of the driest in recent years. The bed sediment consisted mainly of gravel materials and collecting sufficient quantity of the <63 µm fraction for analysis often posed a challenge.

The sediment sampling techniques investigated in this research included; the time integrated sediment tube sampler (Philips *et al.,* 2000) for suspended sediment; Van Veen Grab (United Nation Environment Programme, 2006) for bed sediment; hand scooping with a hand trowel made of stainless steel (Tokalioglu *et al*., 2003) for bank sediment. All sediment samples were collected in sealed transparent polypropylene bags and labelled prior to transport to the laboratory. Water samples were collected using a 500ml high density polyethylene plastic container (USEPA, 2001). Details of these sampling techniques and reasons for their selection are discussed below.

4.1.1 Water sampling

Several methods have been used to collect water samples in rivers. The most commonly used methods are the continuous (automated sampling) and spot (bottle) sampling techniques (Hazelton, 1998). The continuous water sampling usually involves automatic equipment that tests water quality at a given interval, usually hourly. The results obtained using the automatic samplers are reported to be more accurate and reliable than spot sampling since its gives the water condition in real time. Continuous sampling is more effective for monitoring the trend of pollution, most especially in the case of any point source pollution. In comparison to the spot sampling, continuous sampling using an automatic device that is expensive and requires constant checks and maintenance (Madrid and Zayas, 2007); moreover, metal analysis is not possible in automated sampling equipment. Spot sampling is the most commonly used and traditional method for water sampling. It is a widely established and accepted method of water sampling and has been used for regulatory purposes (Allan *et al.,* 2006). A major disadvantage of the spot sampling method is that it does not give much information of any pollution event that might occur on the days when samples were not collected (Allan *et al*., 2006). However, in this study the water samples collected were used to compare the concentration of selected heavy metals to the concentration in sediment collected at the same time.

A common spot sampling technique was used in collecting water samples (Hazelton, 1998; Madrid and Zayas, 2007; Enviroment Agency, 2012). Water samples were collected into 500mL high density polyethylene plastic containers that had been cleaned with 10% v/v nitric acid for 24hours and rinsed with deionised water. The containers were rinsed twice with the river water prior to sample collection. The

samples were collected by submerging the plastic containers into the river facing the direction of flow. Water samples were subsequently tested to determine the concentration of selected heavy metals (Cd, Cu, Ni, Pb, and Zn). Three water samples were collected during sampling, one from each of the three sampling points - left (1m from left bank), middle (3m from left bank) and right (1m from right bank) section of the sampling location.

4.1.2 Sediment sampling

The sediment sampling techniques that were used in this study include the time integrated sediment tube sampler described by Philips *et al.* (2000) for suspended sediment; the Van Veen Grab as described in the United Nation Environment Programme (2006) for bed sediment and a hand scooping method using a stainless steel hand trowel as described by Tokalioglu *et al*. (2003) for bank sediment. All sediment samples were transferred to air-sealed transparent polypropylene bags immediately after collection. External sources of metal contamination were avoided by using sediment samplers made of stainless steel and plastic material (Mudroch and Macknight, 1994).

4.1.2.1 Suspended sediment

It is widely documented that suspended sediment rather than the bed and bank sediment can be used to monitor recent contaminant stress in the aquatic environment (Ongley, 1982). However, higher uncertainties have been associated with sampling suspended sediment in comparison to the bed and bank sediment (Ingersoll *et al.,* 1997). Several methods of sampling suspended sediment have been devised over the years. These methods of sampling can be grouped into three main types: Integrated sampler, instantaneous samplers and pumping samplers (Horowitz, 1991). The integrated suspended sediment sampler collects suspended sediment samples over a period of time. An example is the time integrated suspended sediment sampler described by Russell *et al.* (2000) and the sediment trap described by Gardner *et al.* (1997). The **trap sampler** collects suspended sediment by trapping suspended sediment into containers such as cylinders, funnels, basins or wide base bottles as river velocity decreases as water passes through the container (Gardner, 1980; Gardner *et al.,* 1997). The instantaneous sampler collects bulk water samples containing sediment by sealing off the ends of a flow-through chamber (Horowitz,

1991). The **manual bulk water sampling** collects sediment and water mixture using a bucket (Gray and Gartner, 2009; Roseen *et al.,* 2011). Analysis is carried out for both the filtered (water sample) and unfiltered (sediment + water) samples and the difference is usually taken to be the concentration of contaminants in the suspended sediment (Horowitz, 1995)**.** The **automatic pump sampler** is mainly used for systematic or frequent collection of suspended sediment (Horowitz *et al.,* 1992). Sediment samples are collected at regular interval by pump action or triggered by increases in river velocity or stage (Horowitz *et al.*, 1992; Roseen *et al.,* 2011). **The continuous flow centrifuge** (Rees *et al.,* 1991; Droppo and Jaskot, 1995) is an example of using a pump action for sampling sediment. The continuous flow centrifuge method of suspended sediment sampling is carried out by centrifuging a large amount of sediment-water mixture. Suspended sediment settles at the base of the centrifuge tube and the water (supernatant) is usually pumped back into the river. This method of suspended sediment sampling is mainly limited to bulk collection of suspended sediment due to changes in water chemistry during centrifugation (Ongley and Blachford, 1982). The main advantage of the automatic pumping system is that it can be used in a sampling area with limited access or remote location, samples can be collected during high river velocity and it requires less manual input (Eads and Thomas, 1983; Edwards and Glysson, 1999; Horowitz *et al.,* 1992).

Suspended sediment from the Ravensbourne River was collected using the Time Integrated Sediment Tube Sampler (TISTS) as described by Philips *et al*. (2000), Russell *et al.* (2000) and McDonald *et al.* (2010) because it provides an inexpensive and practical method of collecting representative suspended sediment samples. The TISTS is considered to collect the most representative sample of fluvial suspended sediment (Horowitz, 1991; Russell *et al.,* 2000), presents a cost effective method of collecting suspended sediment compared to the pumping sampler, and since the daily velocity of the Ravensbourne was low, sediment collection was needed over a period of time rather than instantaneously to collect sufficient sample for analysis. The TISTS effectively sample active suspended sediment without disturbing the overlying water, and are easy to use. The main disadvantage is that it is labour intensive and time consuming, and the amount of sediment collected is determined by the river flow condition between installation periods.

The integrated tube sampler was made from a 1m PVC (polyvinylchloride) tube, closed by a threaded PVC cap with an internal O-ring seal. A 50mm hole was drilled at the centre of the top cap for attaching a polyethylene funnel. The base of the funnel was installed with a 4mm opening (for inlet flow) made from laboratory pipette tips. The base of the tube was closed by a second threaded PVC (with internal O-ring seal) cap drilled with a 4mm hole for outlet flow (Figure 4.1).

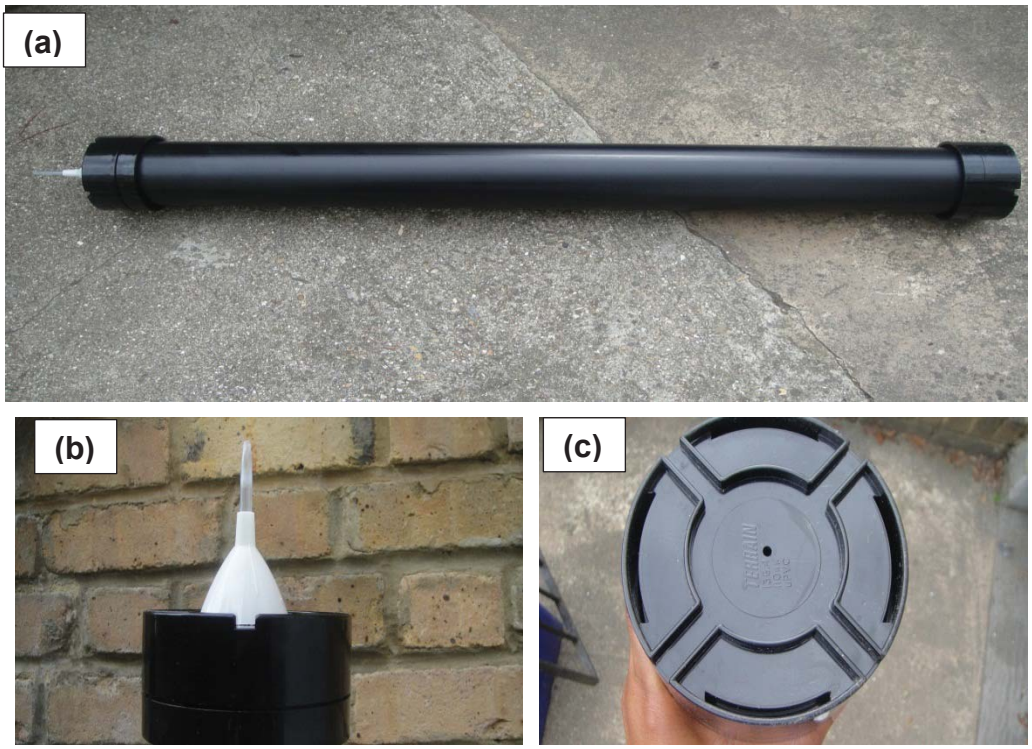
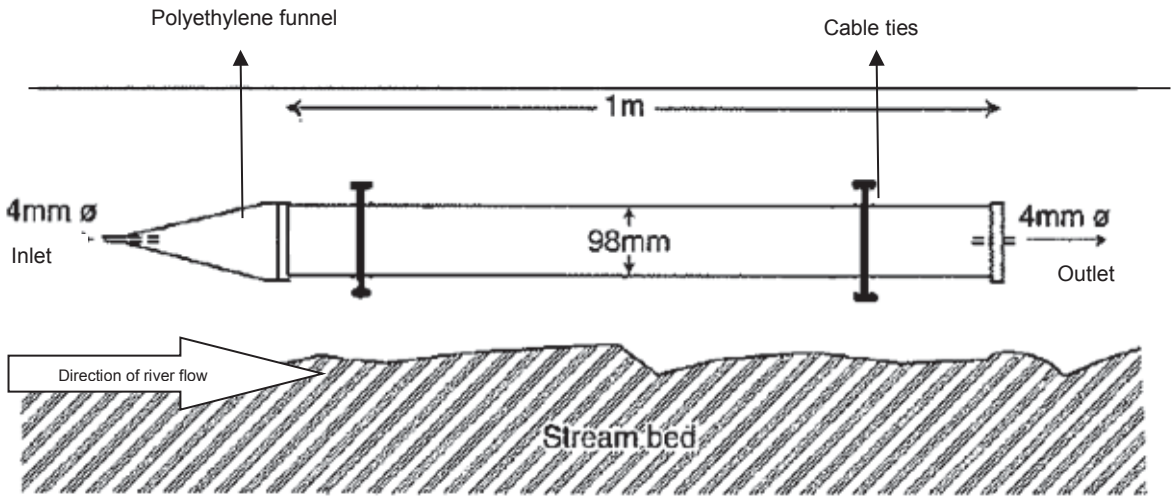


Figure 4.1 Description of the Time Integrated Suspended Tube Sampler (TISTS) (a) Tube sampler (b) top of TISTS (c) base of the TISTS

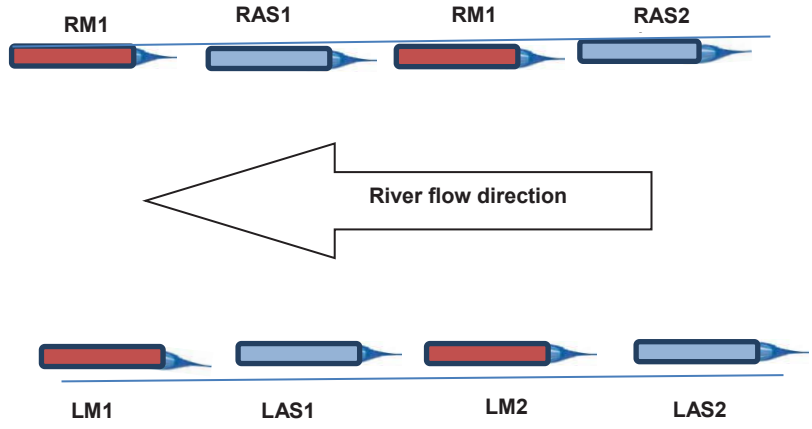
Each sampler was installed horizontally at approximately 0.1m above the river bed at the sampling point, and fastened with cable ties to the wooden revetment along the bank of the River at Ladywell Fields (Figure 4.2). Eight suspended samplers were installed parallel to direction of the river flow, four for the non-storm event and the other four for storm event. The bases of the funnels (4mm opening) were facing upstream.



(Modified from Russell *et al.*, 2000)

Figure 4.2 A cross section of the time integrated suspended tube sampler

The suspended sediments were sampled monthly to allow an adequate quantity of sediment to be collected for analysis. The TISTS collected suspended sediment under different flow conditions between the month of September 2010 to December 2011, and after a storm event in May, 2012. Fluvial sediment was collected from duplicate suspended samplers installed on opposite sides (right and left) of the river, making a total of four TISTS samples each month. A second set of four suspended samplers were installed on opposite sides of the sampling point for sediment collection during a storm event (Figure 4.3)



LM - left monthly, **RM -** right monthly, **LAS -** left after storm**, RAS -** right after storm

Figure 4.3 Position of the Time Integrated Sediment Tube Samplers in Ravensbourne River

4.1.2.2 Bed Sediment

Sediment grabs, sediment corers and dredges are the most commonly used methods for collecting bed sediments for chemical analysis (Förstner and Wittmann 1981; Horowitz, 1991). Dredges are used to collect large sediment samples in deep rivers. Sediment corers collect a vertical section of the bed sediment to a given depth, and are mainly used to monitor historical trends in sediment pollution. However, this research aims to monitor current status rather than historical trends. In comparison to the grab and dredges, the corer creates the least disturbance of bed sediment during sample collection (Horowitz, 1991). A major disadvantage of the corer is that it is not effective in sampling sandy or gravel bed sediment (Palmer, 1984). Some of the most commonly used core samplers are freeze corers, box corers, gravity corers, piston corers and vibrocorers (Horowitz, 1991).

The grab sampler is effective where sediment coring is problematic or impossible due to a gravel or sandy sediment bed. The sediment grab samplers consist of jaws which open as they are lowered into the river bed and close to trap sediment as the grab sampler is pulled out of the river. The various types of grab sampler used in collecting bed sediment include the Ekman-Birge grab, Ponar grab, Shipek grab sampler, Peterson grab, Van Veen grab and the Smith-McIntyre grab (Förstner and Wittman, 1981; Horowitz, 1991). The major differences between the grab samplers are in the jaw design, the capacity and application in soft or gravel bed (International Atomic Energy Agency, 2003).

Most of the bed sampling devices are bulky, labour intensive and usually require more than one operator. The stainless steel Van Veen grab (Van Walt limited) sampler was used in collecting bed sediment sample from the Ravensbourne River due to its ease of use, effectiveness in shallow rivers, portability and light weight (Mudroch and Azcue, 1995) (Figure 4.4). The surface layer of bed sediment was collected to a depth between 5 and 10cm. The stainless steel Van Veen had a 0.5litres capacity and a total weight of 5kg. Bed sediments were collected in July, 2010, between January 2011-December 2011 (except in the month of February and March 2011 due to high river level), and in May 2012 (storm sample).

Figure 4.4 Bed sediment sampling using the Van Veen Grab

4.1.2.3 Bank Sediment

Hand scooping using a spoon and hand trowel is the most widely used method for sampling bank sediment (Rotman *et al*., 2008; Juracek and Ziegler, 2009). The bed and suspended sediment are usually the main sediment compartments investigated with respect to sediment quality in the aquatic environment. However, bank sediment monitoring is important when the source and the transportation of sediment and contaminants (heavy metals) in river systems are investigated. A hand trowel was used to collect sediment samples from the top 10cm layer of the bank at the sampling location (Wang and Chen, 2000). The hand trowel used was made of stainless steel material to avoid contamination arising from corrosion, 15cm wide and 30cm long with a wooden handle. A minimum of four sub-samples with approximately the same mass were collected from randomly selected points within the sampling location to form one composite sample. Bank sediments were collected monthly at the same time as bed sediment samples.

4.2 Field measurement of environmental parameters in the water column

The physicochemical characteristics of the water column were measured on site to avoid any changes that might occur in the water properties in the course of sampling and transportation. The pH, temperature, dissolved oxygen and river discharge were measured using the operational instructions for water sampling provided by the Environment Agency (Bass *et al.,* 2008). A VWR pH and temperature meter (pH 110)

was used to measure river pH and temperature. An Extech dissolved oxygen meter was used to measure dissolved oxygen, electromagnetic current meter (SENSA) was used to measure the river velocity, and a Stanley measuring tape (25ft blade length) was used to measure the river depth. All equipment was calibrated according to the manufacturer's instructions prior to use, and all data were recorded on a field data logging sheet (appendix 2).

The temperature and dissolved oxygen were expressed in degrees Celsius (^{0}C) and milligrams per litre (mg^{-1}) respectively, and the river depth and discharge (flow) were expressed in metres (m) and litres per second (ls^{-1}) respectively. Three water samples were collected, one from each of the three water sampling points. River discharge was calculated from river velocity and cross sectional area of the river.

River discharge = river velocity x cross sectional area.
Where, cross sectional area = average river depth x river width.

4.3 Sample transportation and storage

All sediment samples were placed in labelled and sealed polypropylene bags, and together with water samples were placed in an ice box immediately after collection. The sediment and water samples were stored and transported to the laboratory in the dark at ≤ 4^{0}C in an ice box (Palmer, 1984, USEPA, 2001). The water samples were preserved and stored at 4^{0}C in a refrigerator and the sediment samples were stored at room temperature in air tight plastic bags after drying and sieving.

4.4 Sample preparation

All glassware used in experimental analysis was of grade 'A' standard, and all reagents used were of analytical grade (Aristar and AnalaR grade) unless otherwise stated. High purity deionised water (18.3MΩ) obtained from Milli Q filtration unit was used throughout. All equipment and apparatus were acid cleaned in 10 %(v/v) nitric acid and rinsed with deionised water prior to use. All analyses were carried out within one month for water samples and six months for sediment samples (USEPA, 2001).

4.4.1 Water samples

The water samples were filtered using 0.45µm Stericup Durapore polyvinylidene fluoride (PVDF) disposable filtration units and preserved with 2ml of concentrated nitric acid before storing in a refrigerator at 4^0C until analysis (USEPA, 2001; Environment Agency, 2012).

4.4.2 Pore waters

The effectiveness of sampling pore water, the extraction methods used in analysis and collecting sufficient volume of pore water for analysis remains a challenge (Carr *et al.,* 2001; Simpson *et al*., 2005). Squeezing and centrifugation are the most common methods of collecting pore water (USEPA, 2001). Centrifugation presents a more simple method for retrieving pore water and the most used laboratory method (Mudroch and Azcue, 1995; SETAC, 2001). Selected bed sediment samples were placed in 50ml high density polyethylene centrifuge tubes and centrifuged at 5000rpm for 30mins (Bufflap and Allen, 1995). The centrifuged water sample was filtered using 0.45µm Stericup Durapore polyvinylidene fluoride (PVDF) disposable filtration units. The filtrate was preserved with concentrated HNO_3 (50µl per ml) and stored at 4^0C in refrigeration until analysis.

4.4.3 Sediment samples

4.4.3.1 Sediment drying

Large debris, including plant and gravel-sized material, was carefully removed from sediment samples before sieving (see below). The sediment samples were spread on a glass Petri dish and oven dried to dryness (until a constant weight was determined by weighing) at 105^0C for a minimum of 24hrs using a Gallenkamp oven prior to sieving and analysis (Tessier *et al.,* 1979; Quevauviller, 1998).

4.4.3.2 Sediment Sieving

Endecotts laboratory test sieves were used for dry and wet sieving of all sediment samples. The Endecotts sieve mesh sizes used were <63µm,125µm, 250µm, 0.5mm, 1mm, 2mm, 4mm, 8mm and 16mm. The <63µm and the 2mm are the most common fractions in sediment sample preparation and analysis (Horowitz, 1991;Charlesworth and Lees, 1999b; Byrne *et al*., 2010), and these were

predominantly used in this study. The <63µm is the preferred fraction because it is often associated with high contaminant levels; is not altered by sieving; the fraction that is most easily transported in rivers; and is a major source of food to benthic organism (Förstner, 2004). However the mass of the <63µm fraction is relatively small compared to the 63µm -2mm fraction (Horowitz, 1991), especially in this study. Sieving was only carried out for bed and bank sediment.

Dry Sieving: The sediment samples taken in July, 2010 were dry sieved into different size fractions : <63µm, 63µm-125µm, 125-250µm, 250µm-0.5mm, 0.5-1mm and 1-2mm fractions to study the relationship between heavy metal concentration and particle size, and to compare the metal load contribution of each of the size fractions in both the bed and bank sediment.

The weight of the different size fractions in the sample was determined by weighing each fraction using Sartorius balance CPA Analytical Balance CPA224S-PCE (± 0.001). Results were expressed as percentage against the total weight of the sediment sample. The sieved sediment fractions were homogenised in an agate mortar and pestle and stored at room temperature in air sealed plastic bags for a maximum of six months.

The bed and bank sediment samples were only dry sieved into the <63µm and the 63µm-2mm fraction for metal and other analysis.

Wet sieving: Wet sieving was carried on selected sediment samples using the stainless steel Endecotts laboratory test sieves (USEPA, 2001). Sediments were spread over the 2mm mesh size sieve and washed with deionised water until the rinsate or wash water becomes clear (Drake, 1999). The sieved sediment fraction was then spread on the 63µm mesh size sieve and washed with distilled water until no further sediment was washed through the sieve. The sieved fractions (<63µm and 63µm - 2mm) were centrifuged at 3000rpm for 15 minutes. The supernatant was discarded and the wet samples were spread on glass Petri dishes and oven dried at 105^0C until a constant weight was achieved. After drying, the sediment samples (<63µm and the 63µm-2mm) were homogenised using an agate mortar and pestle and stored in plastic bags at room temperature prior for heavy metal analysis .

4.5 Sediment particle size analysis

The particle size analysis of sediment samples was carried out using a Malvern MS2000 (Hydro 2000MU) Laser Diffraction Particle Size Analyzer (Sperazza *et al.,* 2004) in the Department of Environmental and Geographical Sciences at the University of Northampton. Sediment samples were pre-treated with 30% (v/v) hydrogen peroxide for 24hours at room temperature to remove organic matter following the method of Gray *et al.*, (2010). Approximately 2±0.01g of sediment was weighed into 50ml disposable centrifuge tubes and 20 mL of 30 % (v/v) H_2O_2 was added to each tube. The tubes were loosely capped and allowed to effervesce for 24hrs at room temperature. After the reaction was complete, the H_2O_2 was decanted and the sediment was rinsed with 50mL of deionised water. The mixture was centrifuged at 3000rpm for 10 min and the supernatant was discarded. The rinsing process was repeated with 50mL of deionised water and the supernatant was again discarded. The residue (wet sediment) was transferred into the Malvern sample dispersion unit (Hydro 2000) containing 600mL of ultrapure water produced by a reverse osmosis plant. Each sediment sample was analysed in triplicate to ensure dispersion or aggregation of sediment had not occurred during the measurement process. Summary statistics obtained from this analysis included the median particle size (d50µm- measure of central tendency), d10µm (the diameter in microns containing the smallest 10% of the particle size distribution, i.e. 10% of the sediment size lies below the d10), d90 (90% of the sediment size lies below the d90), the span (the sorting index which gives information on how well sorted the samples are) and the specific surface area (SSA) of particle size were processed by the Malvern 2000 particle size analyser. The particle size results are expressed in µm for d10, d50 d90, and m^2g^{-1} for the specific surface area.

4.6 Total metal extraction analysis

4.6.1 Water samples

The concentrations of selected heavy metals, including cadmium, lead, copper, nickel and zinc in filtered and acidified water samples, were analysed using inductively coupled plasma mass spectrometry (Agilent 7700x ICP-MS) (Peng *et al.,* 2004). Multi-elemental standards CCS-6 (Inorganic Ventures Inc.) were used for calibration. CCS-6 is a trade name of the mixed standards. CCS-6 contains Cd, Cu,

Ni, Pb and Zn. Calibration standards contained 1-100 ppb (1, 5, 10, 50 and 100ppb) of all elements in 2%HNO_3. The following isotopes were used: 60Ni, 63Cu, 66Zn, 111Cd. Pb was determined as an average of ^{206}Pb, ^{207}Pb and ^{208}Pb. All isotopes were analysed in He mode of the collision cell. The 115In was used as an internal standard for Cd, Pb and 103Rh was used as an internal standard for all other metal isotopes. Instrument drift was monitored by running a 1 ppb mixed (Cd, Cu, Ni, Pb, Zn) standard every 10 samples. A 2% (v/v) HNO_3 was used to rinse the auto sampler three times after analysing all standards prior to analysis of samples. The commonly used metal isotopes are 111Cd, 63Cu, 60Ni, 206Pb and 66Zn. The concentrations of heavy metals were reported in parts per billion (ppb).

4.6.2 Pore water samples

Pore water samples were analysed for metals using the inductively coupled plasma mass spectroscopy after filtering and acidifying. The same standards and blanks used in the water sample analysis were used.

4.6.3 Sediment samples

Several methods have been applied in the testing of heavy metal concentrations in sediment such as the Tessier *et al*., 1979 and the Environment Agency (2006) methods. The Tessier *et al*. (1979) involves the use of hydroflouric acid (HF) which is a toxic acid, and the Environment Agency uses a combination of less toxic acids such as aqua regia-1HNO_3:3HCl) (Environment Agency, 2006). In order to compare the effectiveness of using aqua regia for total heavy metal analysis in sediment, the first set of sediment samples collected in July 2010 were analysed using the HF/$HClO_4$/HNO_3 method (Sun *et al.,* 2001; Wen *et al.,* 1997) and the aqua regia method (Environment Agency, 2006) Subsequent sediment samples were analysed using aqua regia because a good agreement of results was achieved for most of the selected heavy metals.

Digested samples were analysed using a Varian VISTA PRO Inductively Coupled Plasmas Atomic Emission Spectrophotometer (ICP-AES). The analytical/elemental lines used were 226.502nm or 228.802nm for Cd, 213.598nm or 324.754nm for Cu, 230.299nm or 231.604nm for Ni, 217.000nm or 220.353nm for Pb, 213.857 for Zn and 185.9 for P. A calibration curve for the ICP-AES was obtained from standard

solutions of heavy metals at concentrations of 0.2ppm, 1ppm, 2pmm, 5ppm, 10ppm, 20ppm, 100ppm in 2%(v/v) HNO_3 and a blank (distilled water). Instrument drift was monitored by running a 5 ppm mixed standard solution (Cd, Cu, Ni, Pb, Zn, P) after every 10 samples, and 2% (v/v) HNO_3 was used to rinse the auto sampler three times after analysing all standards to avoid contamination of sediment samples from the high standards concentration prior to analysis of samples. Equipment drift was adjusted by re-running the standard solutions. The results were reported in milligrammes per kilogram sediment (mg/kg) of triplicate measurements.

4.6.3.1 HF/$HClO_4$/HNO_3 digestion

The HF/HCO_4/HNO_3 total metal extraction was carried out as described by Sun *et al.* (2001) and Wen *et al.* (1997). Triplicate sub-samples 0.1g ± 0.001g dry weight of sediment were weighed (Sartorius balance CPA Analytical Balance CPA224S-PCE) into 100ml Teflon tubes. Four mL of concentrated HF followed by 2mL of concentrated $HClO_4$ were added to the sample and the mixture was heated at 100^0C for 4hrs in a fume cupboard using the Environmental Express SC100 36-well hot block. The temperature was increased to 150^0C to allow the evaporation of the $HClO_4$. The samples were removed from the hot block upon dryness. After cooling to room temperature, 1mL of concentrated HNO_3 and 4ml of deionised water was added; the solution was heated at 60^0C for 20mins or until the solution was clear. The solution was allowed to cool at room temperature and made up to 100ml with deionised water before analysing for Cd, Cu, Ni, Pb, Zn and P (for selected sediment samples) using the ICP-AES. The LGC 6187 (river sediment obtained from the River Elbe close to the Czech-German border) certified reference material was used for quality control- to measure the accuracy and precision of the digestion method (Soares *et al.,* 1999). The LGC 6187 is very stable and accredited by the United Kingdom Accreditation Service (UKAS). It is certified for the heavy metals selected for this study and ICP-AES analysis. It is also used by other researchers in monitoring heavy metal concentrations in sediment (Gaudino *et al*. 2007; Rothwell *et al.,* 2007; Dabrin *et al.,* 2013). The analytical error in the analysis of the reference material was within 10% of the certified concentration of heavy metals. A laboratory control of 5ppm was used to monitor equipment drift. The results were expressed in milligram per kilogram (mg/kg) of dry weight sediment.

4.6.3.2 Aqua regia digestion

The aqua regia digestion method is a simpler method for sediment digestion and involves the use of less toxic acids compared to the $HF/HClO_4/HNO_3$ total extraction method. This is the method used by the Environment Agency for total metal digestion (Environment Agency, 2006). The aqua regia consists of 1:3 v/v of concentrated HNO_3 and concentrated HCl. Sediment (1g±0.001g) was weighed in triplicate (to monitor precision) into 50mL Teflon tubes, 2.5ml of concentrated HNO_3 and 7.5mL of conc. HCl was added to the sample, the tubes were loosely covered and the solution was allowed to stand at room temperature ($<25^0$C) for 8hrs. The solution was then placed on a heating block (Environmental Express SC100) and cap with a reflux condenser flask. It was heated to 60^0C for 10mins, 80^0C for 10mins, 100^0C for 10mins, 160^0C for 2hrs, and allowed to cool for 30mins. Upon cooling, the inside of the condenser flask was rinsed with deionised water into a Teflon tubes. The content was transferred to a 50ml centrifuge tube and made up to 50ml with deionised water. The solution was centrifuged at 3000rpm for 30mins and analysed for the selected heavy metals using 1CP-AES. The results were also expressed in milligrams per kilogram (mg/kg) of dry sediment weight.

4.7 Sediment sequential extraction and analysis for metals and phosphorus

Various methods have been applied in the speciation of heavy metals in sediment (Tessier *et al*., 1979; Maiz *et al.,* 1997; Quevauviller *et al*., 1997; Tokalioğlu *et al.,* 2000; Zimmerman and Weindorf, 2010). The major disadvantages of sequential extractions are they are operationally defined (that is the quantity of heavy metal extraction is dependent on the extracting solution used). The other disadvantages include the redistribution and reabsorption of heavy metals between phases, labour intensive and time consuming experiment and the lack of comparability and quality control (Quevauviller *et al.,* 1997). Despite various criticisms, sequential extraction has gained wide application and acceptance as a method for analysing the distribution of heavy metals in sediment for over 30years.

4.7.1 Choice of sediment sequential extraction method and standards

The Tessier *et al*. (1979) sequential extraction is the most widely used method for metal speciation in sediment. Most of the sequential extraction experiments were

modified from the Tessier *et al.* (1979) method, which takes a minimum of 17.5 hours for completion (Tessier *et al.,* 1979; Zimmerman and Weindorf, 2010). Maiz *et al.* (1997) however developed a short sequential extraction method that lasted for 6hours. The Maiz *et al.* (1997) method obtained similar results for heavy metal speciation in soil samples to those using the Tessier *et al*. (1979) method and the Community Bureau of Reference (BCR) method as described by Ure *et al,* (1993). The Community Bureau of Reference (BCR) sequential extraction was developed by the European Commission as a harmonised method for determining metal speciation in sediment, and various certified reference materials have also been developed for this method (Quevauviller *et al.,* 1997; Tokalioğlu *et al.,* 2000). The BCR sequential extraction differs from the Tessier *at al.* (1979) method by combining the exchangeable and carbonate phase as a single phase (Zimmerman and Weindorf, 2010), and the BCR sequential extraction takes a minimum of 51 hours for completion, about thrice the time it takes to complete the Tessier *et al.* (1979) method. The Maiz *et al.* (1997) and Tessier *et al*. (1979) methods were used in this study to assess the distribution of selected metals in sediment samples, and to compare the differences in metal speciation using different extraction techniques and solutions. The Tessier *et al.* (1979) sequential extraction partitions metals in sediments into five binding fractions - exchangeable, carbonate bound, iron/manganese oxide bound, organic bound, and residual fractions, while the Maiz *et al.* (1997) method partitions metals in sediment into three binding fractions – exchangeable, mobilisable and residual fraction.

There were no specific certified reference materials (CRM) developed for the Tessier *et al.,* 1979 method and the CRM used by Maiz *et al*., 1997 was soil material since the method was originally developed for soil analysis. The Community Bureau of Reference (BCR) 701 certified reference material was used for measuring the accuracy of the sequential extraction experiments as used by previous writers (Pueyo *et al*. 2001; Quevauviller, 2002; Tokalioğlu and Kartal, 2006). The BCR 701 was developed by the BCR for sediment analysis, and known concentrations of each element in the different speciation forms are provided. All results from the sequential extraction experiments were expressed in mg/kg of dry sediment weight.

4.7.2 Maiz *et al.* (1997) Sequential Extraction

Sediment (3g ± 0.001g) was weighed in triplicate into 100mL Teflon tubes. The exchangeable fraction was extracted with 10mL of 0.01M $CaCl_2$ solution at room temperature (<25^0C) for 2hrs on an orbital shaker (Stuart Scientific Incubator with orbital shaker-S150) agitated at 250rpm. The resulting solution was made up to 50mL in disposable centrifuge tubes and centrifuged at 3000rpm for 10mins, and the supernatant was analysed for the selected heavy metals using the ICP-AES. The mobilisable (carbonate, Fe/Mn and organic matter phase) fraction was extracted by adding 2mL of a mixture of 0.05M diethylene triamine pentaacetic acid (DTPA) + 0.01M $CaCl_2$ + 0.1M Triethanolamine (TEA) aqueous solution (pH 7.3) to the residue from the exchangeable fraction. The solution was agitated at 250rpm for 4hrs at room temperature using an orbital shaker. The content was transferred into 50mL disposable centrifuge tubes and centrifuged at 3000rpm for 10mins. The supernatant was decanted and made up to 50mL with deionised water before analysing using ICP-AES. The analytical lines/elemental wavelengths for all the selected elements were similar to that for the total metal extraction. These were 214.4nm and 226.502nm for Cd, 324.754nm for Cu, 231.604nm and 341.4nm for Ni, 216.9nm and 220.3nm for Pb, 206.2nm for Zn and 178.2nm for P. Calibration curves were obtained from standard solutions (0.2ppm, 1ppm, 2ppm, 5ppm, 10ppm, 50ppm, 100ppm in the same matrix of each chemical phase) and blanks (consisting of deionised water) prepared for each extraction phase. Equipment drift was monitored with a 5ppm laboratory control. The residual fraction was calculated as the difference of the sum of the exchangeable and mobilisable fractions.

4.7.3 Tessier *et al.* (1979) Sequential Extraction

Homogenised sediment (1g ± 0.001g) was weighed in triplicate into 100mL acid washed Teflon tubes. The different phases were extracted using 8mL 1M $MgCl_2$ (pH 7) agitated at room temperature for 1hr (for the exchangeable fraction) and 8ml of 1M NaOAc at pH 8.2 with continuous agitation with an orbital shaker at 250rpm at room temperature for the carbonate fraction. This was followed by adding 20mL of 0.04M NH_20H-HCl in 25% (v/v) HOAc was added to the residue from step 2 (the carbonate phase), the mixture was heated at 96 ± 3^oC in a hot bath with occasional agitation to obtain the Fe/Mn fraction. The organic fraction was extracted using 3mL

0.02M HNO_3 + 5ml 30% v/v H_2O_2; the mixture was adjusted to pH 2 with 0.01M nitric acid and heated at 85^0C for 2hrs with occasional agitation using an orbital shaker. An additional 3mL of 30% v/v H_2O_2 was added to the mixture and heated at 65^0C for 3hrs with intermittent agitation using an orbital shaker. The mixture was allowed to cool before adding 5mL of 3.2M NH_4OAc in 20% (v/v) HNO_3; the solution was diluted to 20mL with deionised water and agitated continuously with an orbital shaker at room temperature (<25^0C) for 30mins. The residual fraction was digested with a 5:1 mixture of concentrated HF and $HClO_4$ and heated near to dryness. A 10:1 mixture of HF and $HClO_4$ was subsequently added and evaporated to dryness. Finally 1mL of $HClO_4$ was added to the residue and the mixture was heated until the appearance of white fumes. The remaining residue was dissolved using 1-2mL of 12N HCl and diluted to 100mL with deionised water.

The final supernatant from each of phases 1 to 4 (exchangeable, carbonate, Fe/Mn and organic phase) was centrifuged at 10,000rpm for 30mins, and diluted to 50mL with deionised water before analysing with ICP-AES. The supernatant from the residual phase was diluted to 100mL with deionised water before analysis with ICP-AES. Calibration standards, laboratory control and blanks were prepared for each phase using the same matrix of extracting solution in the samples. The BCR701 was used as the certified reference material. The results were expressed in mg kg^{-1} of dry sediment weight.

The analytical lines/elemental wavelengths for all the selected elements and phosphorus were similar to that used for the Maiz *et al*. (1997) analysis. Calibration curves were obtained from standard solutions (0.2ppm, 1ppm, 2ppm, 5ppm, 10ppm, 50ppm, 100ppm in the same matrix of each chemical phase) and blanks (deionised water) prepared for each extraction phase. Equipment drift was monitored with a 5ppm laboratory control.

4.8 Total organic matter/organic carbon content

Organic matter plays an important role in heavy metal pollution due to its ability to interact with clay minerals, form complexes with metal ions and sequester heavy metal contaminants (Schumacher, 2002). Loss on ignition (LOI) has been widely

accepted as a standard way of measuring the organic matter/organic carbon content in both soils and sediments (Dean, 1974; Heiri *et al.,* 2001; Santisteban *et al.,* 2004). LOI analysis presents a simple, inexpensive, speedy analysis of large sediment samples and does not involve the use of chemicals in contrast to other methods of measuring organic matter such as the titration method and hydrogen peroxide digestion (Schumacher, 2002; Abella and Zimmer, 2007). During the LOI analysis, the organic matter in sediment samples is destroyed by heating to high temperature and the difference in weight after heating is proportional to the sediment organic matter content. Various ignition temperatures (between 450^0C and 600^0C) have been applied to organic matter/carbon content analysis by loss on ignition (Rothwell *et al.,* 2007); however, the principle remains the same. Different studies have shown that organic matter oxidises at temperature between 450^0C and 550^0C (Heiri *et al*., 2001; Santisteban *et al.,* 2004), however Donkin (1991) reported that there is no added advantage when samples are heated above 450^0C, and Schumacher (2002) reported that the decomposition of inorganic carbon is likely to occur at temperature over 440^0C. The ignition temperature used for this study was 450^0C.

The total organic matter content in the sediment samples were determined by percentage loss on ignition (LOI %) as described by Donkin (1991) and Schumacher (2002). Porcelain crucibles were heated in Griffin furnace at 550^0C for 20 minutes to completely remove moisture from the crucibles. The crucibles were allowed to cool in desiccators. After cooling, approximately 1.5g of finely crushed sediment was weighed in duplicate into the porcelain crucibles. The weight of the crucibles and sediment was recorded before placing the crucibles containing sediment in the oven at 105^0C for a minimum of 12hrs. On completion of the heating, the crucibles containing sediment were allowed to cool in desiccators for an hour. The crucible and sediment was reweighed and the differences in weight were used for the determination of the sediment moisture content. The sediment + crucibles were subsequently placed in the furnace at 450^0C for 12hrs. The samples were allowed to cool in desiccators for 2hrs before reweighing.

The LOI % was calculated using the equation:

$$\text{LOI \%} = \left\{ \frac{A - B}{B - C} \right\} \text{X } 100$$

A = Weight of crucible + sample after 450^{o}C for 12hrs

B = Weight of crucible + sample after 105^{o}C for 12hrs

C = Weight of Crucible after 550^{o}C at 20mins

4.9 X-ray diffraction analysis

X-ray diffraction (XRD) was discovered by Max von Laue, a German scientist who proposed that X-rays interacting with a crystal produces an interference pattern (He, 2009). It is a widely used non-destructive and rapid technique for phase identification/mineralogical composition and crystalline structure of inorganic compounds (Dutrow and Clark, 2013). X –ray diffraction experiment have been used since 1912. These interactions were later expressed mathematically by Lawrence Bragg, currently known as Bragg's law. The Bragg's law is given as:

$$n\lambda = 2d \sin \theta$$

Where,

n = the order of reflection

λ = wavelength of the radiation

d = distance between crystal planes (d-spacing)

θ = half the angle between the incident and refracted beams

An X-ray diffractometer consists of three main units: the sample holder, an X-ray cathode tube where X-ray beams are generated, and an X-ray detector. X-ray diffraction operates on the principle that when a focused monochromatic X-ray beam interacts with a sample, part of the beam is reflected, absorbed, refracted and diffracted at the same wavelength as the incidence beam. The diffracted X-rays are detected and processed as peaks which are converted to d-spacing. The d-spacing and the intensities created when an X-ray beam interacts with the sample generates a unique fingerprint of the mineral phases present in the sample. The distances (d-

spacing) between the planes of the atoms are measured using Bragg's Law. Only the planes oriented at right angles (2θ) to the incidence beam will give observable diffracted peaks.

The Enraf Nonius Powder X-ray Diffractometer coupled to INEL CPS 120 position-sensitive detector (PSD) was used in analysing sediment samples for clay mineral composition. Approximately 1g of finely crushed and homogenised sediment sample was carefully fixed onto the specimen holder and rotated around a fixed axis and X-ray diffraction intensities recorded. Data were collected for 30mins (for phase identification) and 60mins (for quantitative analysis). The X-ray diffraction data was calibrated using silver behanate (NIST SRM 640b) for low angle, and silicon for a wider angle range. Clay mineral standards were run for named minerals that were identified as present in initial data and the quantitative data was calculated from the modelled values of each mineral. The phase identification was analysed using the STOE software which includes the ICDD (The International Centre for Diffraction Data) Powder Diffraction Files (PDF) and a search-match programme for peak identification. The quantitative data were expressed as weight percentage of the phase proportion of each clay mineral.

4.10 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscope is widely used in the study of sediment morphology, structure and chemical composition (Swapp, 2013). The major advantages of the SEM include: high resolution and magnification range, that it is capable of producing three dimensional images of sediment samples; and provides a fast morphological analysis of samples (Reed, 1996; Swapp, 2013). A typical SEM consists of an electron gun, anode, magnetic lens, scanning coils, detectors (secondary detector and back scatter detector) and a computer screen to display images. The SEM uses electrons to produce an estimate of the shape of sediment samples. As high kinetic energy electrons produced by the electron gun are focussed on the sediment sample, the electron beam travels through the anode, magnetic lens and coils field until it hits the surface of the sediment sample. On collision with the sediment samples, the sample emits ranges of electrons such as the back scattered electron, secondary electron and X-ray. These electrons are

converted to signals by the detectors and transmitted as images to the computer screen (Schweitzer, 2013).

The scanning electron microscopy was carried out using the Carl Zeiss Ultra Plus Field Emission SEM. Approximately 1g of finely crushed selected <63μm bed and suspended sediment samples were mounted on an aluminium stub, and the electron beam produced by the electron gun was focused on the sample and selected images were downloaded. The final image was projected on a screen from the detector. Selected bed sediment samples (<63μm bed sediment) were coated with a thin layer of conductive material (carbon) prior to elemental mapping analysis using the SEM.

4.11 Geographical Information System Maps

The possible anthropogenic contribution of selected heavy metals in relation to natural background concentration was investigated. The data on the background concentrations of the selected heavy metals in soil around the sampling location from Bromley (upstream of sampling location) to Deptford (downstream of sampling location) were obtained from the British Geological Society (BGS). The data was plotted into the Geographic Informational System (GIS) software (Archmap 10.1) to obtain a map displaying the concentration of selected metals around the sampling location.

4.12 Statistical analysis

All statistical analysis was carried out using Microsoft Excel spread sheets, GraphPad Prism 5.1 and SPSS 20.0 software. The normality (Gaussian) distribution of the data obtained for heavy metal concentrations in both the water column and sediment was analysed using the Shapiro-Wilk and Kolmogorov-Smirnov normality test due to its appropriateness for small sample size (<50) (Chen, 1971; Field, 2001). The data is normally distributed if the probability value is greater than 0.05 ($p>0.05$) and not normally distributed if the probability is less than 0.05 ($p<0.05$). The results show that most of the data did not follow the Gaussian distribution. For uniformity of data analysis, a non – parametric test was used for all analysis. The Spearman's rho test was used to measure correlations between variables (sediment

specific surface area and heavy metal concentration, and heavy metal concentration between compartments). The Mann-Whitney U non-parametric test was used to compare the mean of metal concentration in the wet and dry sieved sediment. Univariate analysis was used to calculate the mean and standard deviation of repeated measures for each sample, and the non-parametric Kruskal-Wallis one way analysis of variance was used to compare the difference in heavy metal concentration between sediment compartments (bed, bank and suspended sediment). The Dunn (1964) post hoc test originally designed for the Kruskal-Wallis non-parametric test was used to test the pairwise comparison among the bed, bank and suspended sediment samples.

Box plots were used to show the annual median value of each sampling technique; the variation in the annual metal concentration with each sampling technique represented by the interquartile range, (the 75th percentile minus the 25th percentile); and outliers (the presence of anomalous data) (Helsel and Hirsch, 1992).

4.13 Quality control

Working calibration solutions, blank calibration solutions, certified reference materials and an independent/check analytical quality control solution were prepared and analysed alongside digested sediment and water samples Experiments were repeated on random samples on selected samples for the total and sequential extraction experiment. Blank samples and laboratory triplicate samples were used for total metal and sequential extraction experiments. The calibration coefficient of the calibration line (linear fit) was always better than 0.999 for all the analysis, and the equipment drift was within 10%. The replicate analysis for different experiments shows that most experiments had a reproducibility of about ±10%. The certified reference material LGC6187 for total metal analysis was also within ±10% of the certified value which is a good and acceptable experimental limit for reference materials (Table 4.2).

Table 4.2 Experimental values for certified reference material for total metal analysis

LGC 6187	Certified reference value (mg kg^{-1})	Experimental value (mg kg^{-1})	Certified recovery (%)
Cd	2.70	2.47±0.22	91.48
Cu	83.60	80.76±11.42	96.61
Ni	34.70	32.34±3.71	93.20
Pb	77.20	70.97±5.30	91.93
Zn	439.00	428.38±52.37	97.58

There are no specific reference materials developed for either the Maiz *et al.* (1997) or the Tessier *et al*. (1979) sequential extraction method. Although the BCR 701 was originally developed for the BCR sequential extraction method, the BCR 701 certified reference material was however used as part of the quality control in the Maiz *et al* sequential extraction method. The results obtained for the BCR 701 further confirms that sequential extractions are operationally defined. The BCR 701 certified reference material exceeded the ±10% tolerance, mainly because the BCR 701 was originally developed for the BCR method and sequential extraction experiments are operationally defined. The average values obtained for each certified reference material is given below (Table 4.3).

Table 4.3 Experimental values for certified reference material (BCR 701) for sequential extraction analysis

Sequential extraction	BCR 701	Certified reference valve (mg kg^{-1})	Experimental value (mg kg^{-1})	Certified recovery (%)
Exchangeable	Cd	7.34	0.11±0.00	1.50
	Cu	49.30	1.26±0.10	2.56
	Ni	15.40	0.55±0.02	3.57
	Pb	3.18	0.31±0.12	9.75
	Zn	205.00	2.04±0.96	1.00
Mobilisable	Cd	3.77	3.50±0.18	92.84
	Cu	124.00	23.66±0.44	19.08
	Ni	26.60	7.95±0.10	29.89
	Pb	126.00	0.05±0.00	0.04
	Zn	114.00	35.60±0.34	31.23

The percentage recovery was for all metals were very low and exceeded the ±10% acceptable range for all the metals except for Cd in the mobilisable phase which gave a recovery of 92.84% (Table 4.3). The BCR 701 was not used in further experiments. Calibration standards, check analytical quality control solution and blanks were used as quality control in all sequential extraction experiments.

SECTION 2

Results and Discussions

Introduction

This section is divided into five chapters (Chapter 5, 6, 7, 8, 9 and 10). **Chapter 5** describes the results for the water column of the Ravensbourne River including the pH, temperature, river flow, dissolved oxygen and the concentration of the selected heavy metals in the water column. **Chapter 6** shows results for physical characteristics of sediment including particle size distribution, specific surface area, sediment morphology and mineral composition for selected sediment samples for the bed, bank and suspended sediment compartment. **Chapter 7** shows results for heavy metal concentration in the different sediment fractions (<63μm and the 63μm-2mm fractions) and the different sediment compartments. **Chapter 8** provides the results for the fractionation (sequential extraction) of heavy metals in the bed, bank and suspended sediment, and the differences in the results from using two different sequential extraction experiments. **Chapter 9** describes the results for the total concentration and sequential extraction results of phosphorus on selected sediment samples.

Chapter 5
Characterization of the water Column

5.1 Characteristics of the water column at the sampling location

The physical and chemical properties of the Ravensbourne at the sampling location varied across the sampling period (January - December 2011). The results for each field parameter (pH, temperature and dissolved oxygen) are the average of three readings taken at the left, middle and right section of the sampling location. The river depth varied between 0.1m and 0.6m, and was greater on the left side (in direction of flow) of the river. The river temperature ranged from 4^0C to 20^0C over the sampling period with the highest temperature recorded in summer (Table 5.1). The pH and dissolved oxygen levels did not vary much compared to other parameters. The concentrations of all the heavy metals (Cd, Cu, Ni, Pb, and Zn) were in general highest in the months of February to June, tending to increase over this period. The month of June had the highest concentration of all the selected heavy metals compared to the rest of the sampling period and this period saw the highest monthly average rainfall (83.6mm) for the non-storm event samples (Jan.-Dec. 2011) (Table 5.1). There were two storm events (rainfall greater than 30mm/day); however, the storm event of February 2011 resulted in relatively high concentrations of Cd, Cu, Ni, Pb and Zn in the water column. The concentrations of heavy metals in the water column after the storm event of May 2012 were broadly comparable with or lower than those of non-storm samples (Table 5.1).

Table 5.1 Physico-chemical characteristics (mean±SD) of the water column of the Ravensbourne River at Ladywell Fields (n=3)

Sampling Period	Cd, ppb	Cu, ppb	Ni, ppb	Pb, ppb	Zn, ppb	Rainfall, (Deptford) average monthly (mm)	Discharge (Ls^{-1})	pH	Temp (^0C)	DO mg/L)
Sept-10	0.04±0.00	4.80±0.00	6.15±0.64	0.95±0.03	19.73±0.23	52.70	219	8.20	11.90	9.80
Oct-10	0.05±0.00	5.20±0.00	6.05±0.00	1.48±0.00	27.47±1.16	77.50	256	7.90	9.40	10.10
Nov-10	0.22±0.00	16.70±0.00	8.29±0.00	2.87±0.06	67.23±0.12	38.80	129	7.11	7.10	10.40
Dec-10	0.05±0.00	7.52±0.04	5.84±0.00	0.53±0.06	40.09±0.02	31.60	135	7.98	6.60	10.20
Jan-11	0.04±0.01	4.57±0.26	4.95±0.21	0.23±0.19	13.77±1.16	77.60	83	7.60	4.00	10.00
Feb-11	**0.39±0.04**	**60.13±0.67**	8.50±0.19	**41.57±0.50**	**152.97±0.06**	32.40	2370	7.92	9.00	9.40
Apr-11	**0.33±0.00**	**43.83±0.21**	8.33±0.20	**41.47±0.25**	**143.30±0.61**	13.00[a]	260	8.17	12.6	9.10
May-11	**1.58±0.03**	**132.97±3.52**	**24.08±0.03**	**242.03±0.06**	**578.00±11.14**	28.00	224	7.55	13.3	6.90
Jun-11	**2.13±0.12**	**175.97±0.06**	**29.73±0.64**	**332.00±14.73**	**782.00±5.29**	79.80	320	8.13	20.3	8.50
Jul-11	0.23±0.30	6.22±0.03	5.44±0.13	0.67±0.02	79.87±0.32	52.40	173	8.20	16.2	10.10
Aug-11	0.04±0.00	4.00±0.02	3.02±0.02	0.30±0.01	16.00±0.10	66.20	264	7.96	15.4	8.10
Sep-11	0.04±0.00	3.95±0.04	5.12±0.07	0.26±0.03	14.27±0.15	17.00	196	8.05	12.3	6.10
Oct-11	0.04±0.00	5.24±0.31	6.05±0.01	2.02±0.90	27.10±0.36	18.40	332	7.96	11.9	5.00
Nov-11	0.03±0.00	3.71±0.03	5.96±0.17	2.65±0.14	17.9±0.79	25.40	305	7.04	8.5	9.60
Dec-11	0.05±0.01	4.68±0.00	4.75±0.00	3.17±0.24	20.97±0.05	53.80	430	7.07	8.0	8.60
May-12	0.04±0.00	4.69±0.01	4.24±0.12	2.25±0.99	17.27±1.10	118.3[b]	490	6.98	9.1	10.60
Annual Ave. (Jan.-Dec. 2011)	**0.45**	**40.48**	9.63	**60.58**	**167.83**					
Maximum AA - EQS[c] (UK)	**0.25**	**28.00**	**20.00**	**7.20**	**125.00**					

The values in **bold** exceeded the maximum UK EQS value. [a]April rainfall average from 27/02/11 to 19/04/11 as no sampling was carried out in the month of March

[b]Rainfall data from April 5th to May 5th 2012.

The storm event occurred on the 28th of April with a total daily rainfall of 23.5mm; storm sample was collected on the 5th of May, 2012.

[c] **AA –** EQS Annual Average Environment Quality Standards (Source UKTAG, 2008a).

Zinc had the highest concentration of all the metals, followed by Ni, Cu, Pb and Cd. The monthly concentrations of all the heavy metals were well below the United Kingdom annual average environmental quality standards except for the months of February, April, May and June 2011 (Table 5.1). The average concentration (January, 2011-December, 2011) of each heavy metal in the Ravensbourne River exceeded the UK maximum environmental quality standards during the sampling period except for nickel (Table 5.1). There was a strong significant positive correlation between the concentrations of all the metals in the water column (Table 5.2). The correlation was strongest (r>0.9) between Cu and Cd, Cd and Zn, and Cu and Zn. There was a significant positive correlation (r=0.57) between pH and temperature, and a significant negative correlation (r=-0.50) between temperature and dissolved oxygen (Table 5.2). There was no significant relationship between river discharge and rainfall, and there was also no significant relationship between the river discharge and rainfall with the concentrations of all the metals in the water column (Table 5.2).

Table 5.2 Spearman correlation between the average physico-chemical characteristics of the water column of the Ravensbourne River (n=3)

	Cd ppb	Cu ppb	Ni ppb	Pb ppb	Zn ppb	Rainfall (mm)	Discharge (ls^{-1})	pH	Temp (^0C)	DO mg l^{-1}
Cd ppb										
Cu ppb	0.90***									
Ni ppb	0.68**	0.81***								
Pb ppb	0.66**	0.67**	0.70**							
Zn ppb	0.91**	0.94***	0.82***	0.76***						
Rainfall (mm)	0.09	-0.01	-0.16	-0.10	-0.06					
Discharge (l/s)	0.04	0.05	0.05	0.55	0.14	-0.06				
pH	0.25	0.28	0.26	-0.21	0.25	-0.05	-0.28			
Temp (0C)	0.34	0.28	0.25	0.19	0.35	-0.02	0.18	0.57*		
DO mg/l	-0.04	0.01	-0.17	-0.16	-0.04	0.30	-0.31	-0.22	-0.50*	1.00

***p<0.05, **p<0.01, ***p<0.001**

A comparison of the concentration of metals in the water samples for the two storm events shows a huge increase in the concentrations of metals in the February storm event. The increase in metal concentration varies with metal. The highest increase in metal concentration was noticed in Zn and Cu which have about 19 and 13 times higher in the February storm sample compared to the May 2012 storm sample (Table 5.1). The concentration of Ni only doubled in the February storm sample.

The river discharge was also higher in the February storm (2370 Ls^{-1}) compared to the river discharge for the May 2012 (490 Ls^{-1}) (Table 5.1). However, the total monthly rainfall was higher in May 2012 (118.30 mm) compared to February 2011 (32.40 mm)

5.2 Pore water

The results indicate that concentration of heavy metals in the pore water from selected samples were higher than the water column (Table 5.3). The month of June had the highest concentration of all the heavy metals in the pore water, when it was also highest in the water column (Table 5.1).

Table 5.3 The concentration (mean±SD) of heavy metals in selected pore water and water samples (n=3)

Pore water/water	**Cd, ppb**	**Cu, ppb**	**Ni, ppb**	**Pb, ppb**	**Zn, ppb**
Jun-11	**13.30±0.70**	**2780.00±155.60**	**240.50±0.70**	**2285.00±49.50**	**5685.00±190.90**
Jun-11	2.13±0.10	175.97±0.10	29.73±0.70	32.00±14.70	782.00±5.30
Sep-11	**0.12±0.00**	**7.13±0.10**	**7.72±0.70**	**0.46±0.10**	**71.40±0.30**
Sep-11	0.04±0.00	3.95±0.00	5.12±0.10	0.26±0.00	14.27±0.20
Oct-11	**0.08±0.00**	**12.95±0.60**	**8.07±0.00**	**8.04±0.40**	**61.25±12.10**
Oct-11	0.04±0.00	5.24±0.30	6.05±0.00	2.02±0.90	27.10±0.40

The figures in **bold** are for pore water, pore water were only collected in the months of June, September and October

As with the water column, Zn had the highest concentration of all the metals and Cd had the lowest concentration. The concentration of heavy metals in the pore water for the sampling months (June, September and October, 2011) mainly followed the order Zn>Cu>Ni>Pb>Cd. The heavy metal concentrations in the pore water exceeded the maximum UK EQS for water column levels for rivers (Table 5.3) for all the heavy metals in the month of June, and the concentration of Pb in the month of October. There was significant difference ($p<0.05$) between metal concentration in the water column and in pore water only for the month of September. There was also a significant correlation ($r=0.93$, $p<0.0001$) between the concentration of metals in the water column and that in the pore water. There was no significant relationship between metal concentration in the pore water and that in bed and

bank sediment for both the <63µm and the 63µm-2mm particle sizes (See Chapter 7).

5.3 Discussion

Water samples were not examined in terms of sampling using different techniques, but to study the possible effect of heavy metal contaminated sediment on water quality with respect to the Water Framework Directive. The environmental characteristics of the water such as pH, temperature and dissolved oxygen are known to affect the mobility of metal between the water column and sediment (Eggleton and Thomas, 2004; Atkinson *et al.,* 2007). These environmental factors play a significant role with respect to the release of metals from sediment (Förstner *et al*., 1994; Beck and Sañudo-Wilhelmy, 2007). The pH of the water column of the Ravensbourne River ranges from neutral to slightly alkaline (6.98 - 8.20). At neutral to slightly alkaline pH, heavy metals tend to be associated with the sediment and are usually not mobile unless they are physical disturbed or there is bioturbation (Atkinson *et al*., 2007). Metal release into the water column is suggested to occur mainly at low pH (<6) which is not a common pH reading in most urban rivers in the UK. As with the sample site of the River Ravensbourne most urban rivers have a slightly alkaline pH, for example the River Lee in North East London had a mean pH from 7.2-7.9 (Snook and Whitehead, 2004). The pH of River Wandle in South London and the Hogsmill River in South West London reported a pH of 7.4 and 7.6 respectively (Aquilina, 2013). Although these pH values suggest that most of the heavy metal contaminants should be associated with sediment, the river quality for most urban rivers in London are poor for metal content (Environment Agency, 2013a). The Ravensbourne annual average metal content in the water column exceeded the EQS for 4 of the 5 metals studied (Figure 5.1) The metal concentrations in the water columns of urban rivers including the Ravensbourne could be the result of a continued influx of metals arising from diffuse sources of pollution such as road run-off or unidentified point sources.

Increased temperature is associated with increased biological activities such as bioturbation, and metal remobilization from sediment to the water column increases exponentially as water temperature reaches 20^0C (Beck and Sañudo-Wilhelmy, 2007). Bioturbation can enhance the bioavailability of some metals in surface sediments through the oxidation of acid volatile sulphide (Peterson *et al.,* 1996;

Simpson *et al.,* 2012). From the temperature reading of the Ravensbourne River during the sampling period, biological activities are likely to be highest in the summer months (June - August), as these months had the highest temperature reading ranging from 15.4^0C – 20.3^0C (Table 5.1) and the month of June had the highest concentration of metals in the water column and the pore water (Table 5.1 and 5.3). The probable increase in biological activity does not result in any increase in metal concentration in the water column for the rest of the summer months (July and August). A significant increase in metal concentration only occurred in the month of February to June. As a consequence it seems unlikely that metals released from the sediment by bioturbation were a major source of metals in the water column, again, suggesting diffuse or point source pollution key in this respect. The results obtained for the concentration of Cd, Ni and Pb in the water column at the study location complied with the UK EQS values on priority substances set out in the Daughter Directive in most of the sampling months except for the months of February – June, 2011. Nevertheless the annual average for the majority of metals exceeded the annual average EQS (Figure 1). This could also be due to the storm event of February 2011 where unknown point source pollution was washed down the river.

The range of dissolved oxygen concentration in the Ravensbourne, which is usually classified as medium ($5mgL^{-1}$) to high ($10.60mgL^{-1}$) implies that surface sediment were mostly oxidised during the period of sampling. This often results in oxidised sediment that is capable of adsorbing dissolved metal hence reducing their mobility to the water column. The significant negative correlation between temperature and dissolved oxygen confirms that dissolved oxygen increased with decreasing temperature during the sampling period at the Ravensbourne River (Delpla *et al*., 2009).

Compared to other urban rivers in the UK, the chemical quality of the Ravensbourne River did not show much variation. The concentrations of dissolved Pb, Ni and Cd for the Ribble, Calder and Douglas catchments in North West England were well below the annual average EQS values for all three heavy metals (Rowland *et al.,* 2011). A regional overview of the water quality of the River Lee from 1991-2000 studied by Snook and Whitehead (2004) shows higher heavy metals contamination in the lower reaches of the River Lee in East London. The pH

ranged from 7.5 - 8.3 which is similar to the Ravensbourne, the average concentration of Cd, Cu, Ni, Pb and Zn over the 10 year sampling period showed compliance with the UK EQS values except for Ni, although there were periods when the metals concentration exceeded the UK EQS values (Snook and Whitehead, 2004) as with the Ravensbourne River. This could be as a result of diffuse metal sources commonly from urban road surfaces as suggested for the River Lee (Snook and Whitehead, 2004). The significance of the metals measurements in terms of exceeding any EQS results in poor river quality that not only fails to meet the WFD, but could lead to loss of aquatic life.

It is generally accepted that the concentration of contaminants in pore water is a sensitive indicator of chemical reaction between the water column and sediment column (Burone *et al.,* 2005). Some numerical assessment of the environmental impact of sediment related heavy metal contaminants are based on pore water concentration (Ankley *et al.,* 1991; Burgess *et al.,* 2013; Huo *et al.,* 2013). It may be a more useful measurement of sediment metal contamination since there is likely to be more metal exchange between the pore water and the water column than for sediment bound metals. Certainly sediment dwelling organisms will be exposed to metals in pore water. There was no consistency in the relationship between the concentration of metals in the sediment and water column (see chapter 7) which might imply that sediment was not the major source of metal contamination in the water column.

Chapter 6

Characteristics of the sediment compartment

6.1 Physical Characteristics of Sediment

Three of the most important factors likely to affect the concentration of heavy metals in sediment are particle size, organic matter content and sediment mineralogy which were investigated in this study. Other physical characteristics such as sediment mass and sediment morphology were also considered in this chapter. This chapter examines the physical characteristics of sediment from the different sediment compartments (bed, bank and suspended) and for different particle sizes (<63µm and 63µm-2mm) for samples taken from the Ravensbourne River. The impact of sampling technique and preparation on the characteristics of the sediment collected were also considered.

6.1.1 Sediment mass

The mass of sediment obtained using different sampling techniques is significant in sediment monitoring for quality standards. For gravel beds such as those in the Ravensbourne River, obtaining sufficient mass of the <63µm particle size may present a challenge. The results obtained from dry sieving of the sample collected in the month of July, 2010 for the bed and bank sediment indicated that the silt and clay fraction (<63µm) had the smallest proportion of the total sediment mass, while the sand fraction (63µm-2mm) had the largest for all sediment compartments studied, particularly in the bed sediment (Table 6.1).

Table 6.1 Sediment particle size compositions for bed and bank sediment of the Ravensbourne River at Ladywell Fields collected in July 2010.

Size fractions		River	River	River	River
From	To	Bed (g)	Bed (%)	Bank (g)	Bank (%)
	>16 mm	653.7	19.1		0.0
8mm	16mm	943.6	27.6		0.0
4mm	8mm	529.7	15.5	1.2	0.4
2mm	4mm	296.2	8.7	1.3	0.4
1mm	2mm	153.5	4.5	3.3	1.0
0.5 mm	1mm	204.2	6.0	10.4	3.1
250µm	500µm	488.3	14.3	65.9	19.3
125µm	250µm	134.5	3.9	171.4	50.3
63µm	125µm	12.4	0.4	58.3	17.1
	<63µm	5.6	0.2	28.9	8.5
Total		3421.7	100.0	340.7	100.0

The <63μm fraction consisted of <1% of the total mass of bed sediment and approximately 8-10% of the bank sediment samples collected throughout the month of July, 2010 (Table 6.1). The bed sediment of the Ravensbourne River consisted mainly of gravel (>4mm fraction, approximately 62% of the total bed sediment mass) which are not considered by most authors and regulatory bodies when testing for trace metal concentration in sediment (Hseu *et al.,* 2002; Hudson-Edwards *et al*., 2003; Peng *et al.,* 2004). The <63μm fraction represented only 0.20% of the total sediment particle range whereas the bank sediment composed of 8.50% of the <63μm fraction. Similar results were obtained throughout the sampling period (Table 6.2). The mass of sediment obtained for each sediment compartment throughout the sampling period is given (Table 6.2).

Table 6.2 Sediment mass throughout the sampling period

	LM1(g)	LM2 (g)	RM1(g)	RM2 (g)	Bed <63μm (g)[a]	Bank <63μm(g)[a]
Sep-10	6.0	4.0	4.0	4.0	NS	NS
Oct-10	8.0	4.0	3.0	4.0	NS	NS
Nov-10	4.0	4.0	3.0	4.0	NS	NS
Dec-10	4.0	3.0	3.0	3.0	NS	NS
Jan-11	14.0	4.0	14.0	5.0	6.0	>100
Apr-11	13.0	13.0	12.0	6.0	10.0	>100
May-11	6.0	3.0	3.0	4.0	13.0	>100
Jun-11	7.0	6.0	5.0	4.0	8.0	>100
Jul-11	15.0	13.0	4.0	6.0	7.0	>100
Aug-11	4.0	3.0	3.0	3.0	7.0	>100
Sep-11	4.0	3.0	3.0	3.0	6.0	>100
Oct-11	6.0	3.0	3.0	3.0	10.0	>100
Nov-11	4.0	3.0	3.0	3.0	6.0	>100
Dec-11	5.0	4.0	4.0	3.0	6.0	>100
May-12	23.0	22.0	18.0	16.0	17.0	>100

(a) Indicates the weight composition in approximately 1000g of total sediment samples by dry sieving. NS indicates not sampled.
LM-Left monthly Integrated Sampler
RM-Right monthly Integrated Sampler

Samples taken from the bank sediment always had sufficient sediment mass to allow all the planned analysis to be carried out. The mass of <63μm sediment fraction collected in the bed sediment and suspended sediment were generally insufficient for all the planned laboratory analysis. A higher mass of suspended sediment was also collected in the left monthly integrated samplers compared to the right monthly integrated samplers.

6.1.2 Particle size distribution

The monthly particle size distribution and specific surface area (SSA) varied for the bed, bank and suspended sediment in the Ravensbourne River at Ladywell (Tables 6.3 and 6.4). There were insufficient sediment samples for particle size analysis in some of the sampling months for the <63µm bed sediment and the suspended sediment samples (Tables 6.3 and 6.4).

Table 6.3 Particle size analysis of the bed and bank sediment

	Bed <63µm		Bed 63µm-2mm		Bank <63µm		Bank 63µm -2mm	
Sample	**SSA**	**D50**	**SSA**	**D50**	**SSA**	**D50**	**SSA**	**D50**
Jan-11	a	a	a	a	1.26	10.43	0.71	99.67
Feb-11	a	a	a	a	0.91	15.81	0.21	191.17
Apr-11	0.34	36.69	0.09	465.53	1.31	9.42	0.25	174.05
May-11	1.12	10.54	0.08	332.81	1.16	9.98	0.44	133.12
Jun-11	0.18	220.88	0.02	482.56	0.84	18.75	0.19	176.65
Jul-11	0.55	126.58	0.04	437.58	1.01	13.58	0.24	168.45
Aug-11	0.71	21.61	0.26	189.62	1.02	18.10	0.24	145.41
Sep-11	a	a	0.06	505.04	1.09	13.72	0.25	185.47
Oct-11	a	a	0.06	266.26	1.08	11.15	1.08	130.71
Nov-11	a	a	0.05	402.95	1.14	12.13	0.98	130.60
Dec-11	a	a	0.02	569.69	0.40	52.87	0.16	177.61

a indicates where there was insufficient sample for analysis.

SSA-specific surface area, **D50**- median particle size distribution

Table 6.4 Particle size analysis of the suspended sediment

	LM1		LM2		RM1		RM2	
	SSA	**D50**	**SSA**	**D50**	**SSA**	**D50**	**SSA**	**D50**
Sep-10	1.02	11.85	0.85	17.84	0.58	49.12	0.82	19.11
Oct-10	0.81	20.68	0.82	19.87	a	a	0.49	41.95
Nov-10	0.71	27.86	1.02	11.69	a	a	a	a
Dec-10	0.91	14.73	a	a	a	a	a	a
Jan-11	0.83	17.40	a	a	0.74	22.32	0.65	27.09
Apr-11	0.99	16.20	0.41	77.46	0.54	38.30	a	a
May-11	1.01	11.63	a	a	a	a	0.63	31.24
Jun-11	a	a	a	a	0.53	36.10	0.68	26.64
Jul-11	0.83	16.80	1.13	11.39	0.69	23.26	a	a

a indicates where there was insufficient sample for analysis.

LM Left monthly suspended sampler **RM** Right monthly suspended sampler
SSA-specific surface area, **D50**- median particle size distribution

The results for the particle size analysis showed that grain size was sometimes larger than the filter size especially in the bed sediment. This is mainly due to the shape of the grain size which not spherical (see Figure 6.2 below). A rod like shapes with a larger particle length compared to the width would easily passed through the <63µm mesh sieve aperture. The particle sizes of the bed sediment were larger than those of the bank and suspended sediment in most of the sampling months (Table 6.3). The median particle size (d50) of the <63µm bank sediment was particularly large in the month of December (52.87µm) compared to the rest of the sampling months. However, in general the bank sediment (<63µm) contained a higher proportion of silt and clay compared to the bed and suspended sediment while the bed sediment consisted mainly of sand and gravel (>4mm - which are not considered in this study) materials. The d50 particle sizes for the <63µm bank sediment ranged from 9.42µm - 52.87µm, while the bed and suspended sediment d50 particle sizes ranged 10.54µm - 220.88µm and 11.63µm-27.86µm (for Left monthly 1 suspended sediment sampler) respectively.

There was also substantial variation in the particle sizes for the different integrated tube samplers sampled at the same time, such as in the month of September, 2010 and April, 2011 (Table 6.4). The d50 for RM1 in the month of September, 2010 was more than twice the d50 of the sediment sizes in the rest of the suspended tube samplers. The variation in the chemical characteristics of each sediment sample with respect to heavy metal concentration is shown in chapter 7 and any relationship is discussed there.

The physical characteristics of sediment such as surface area and chemical characteristics such as mineral composition are highly dependent on sediment particle size (Walling *et al*., 2003; Zhao *et al*., 2010).

6.1.3 Sediment surface morphology and crystalline structural composition

The Ravensbourne sediment varied in size and morphology. Sediments usually consist of irregularly shaped particle size (Horowitz, 1991). The optical image obtained for the <63µm bed sediment using the Carl Zeiss Ultra Plus Field

Emission scanning electron microscope indicated that some of the large particles are made up of flocculated aggregates of smaller sediment particles which is very common when sediment are dry sieved (Figure 6.1).

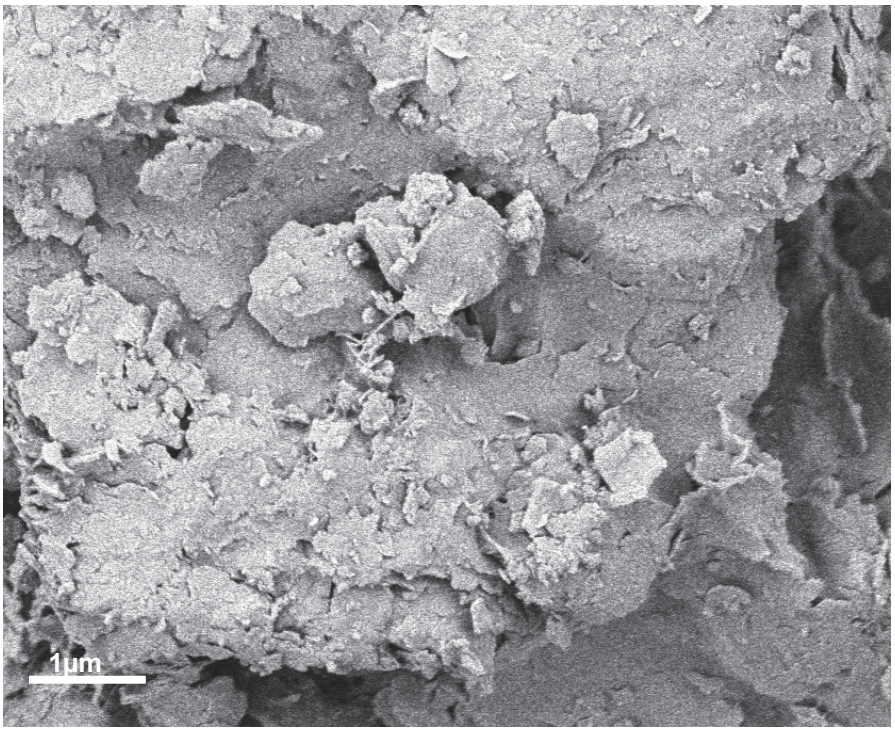
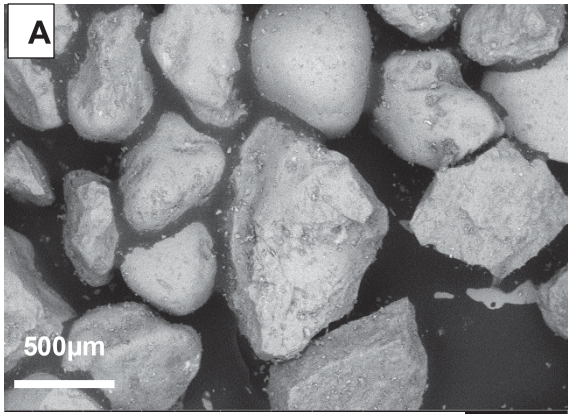
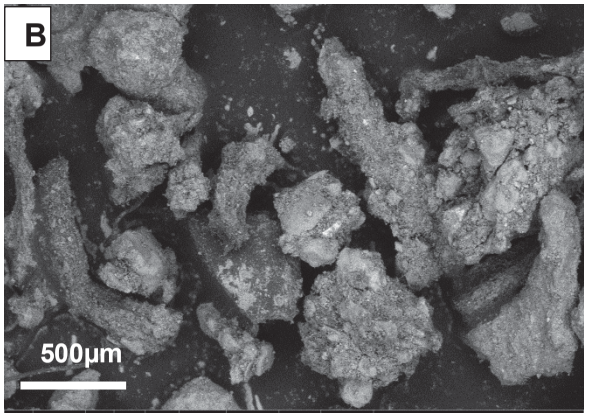


Figure 6.1 The morphology of the <63µm November 2011 bed sediment

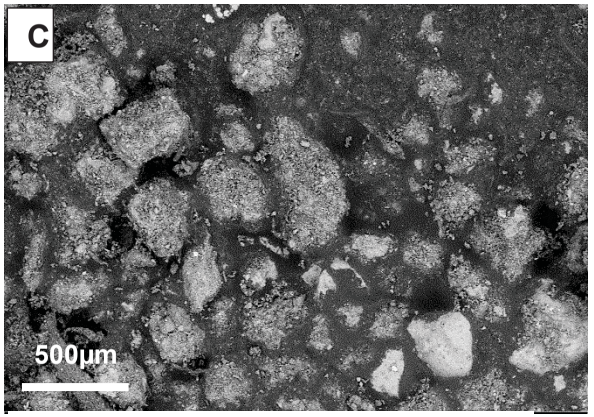
Most of the sediment particles were irregularly shaped and not spherical, and also varied substantially both in composition and size. The shape and structure of the bed, bank and suspended sediment are illustrated below (Figure 6.2). The shapes are similar for all the sediment compartments, plant materials was seen in bank and suspended sediment (Figure 6.2).



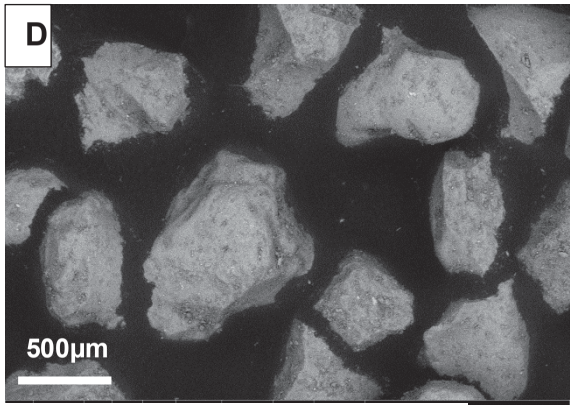
Bed 63µm-2mm January, 2011



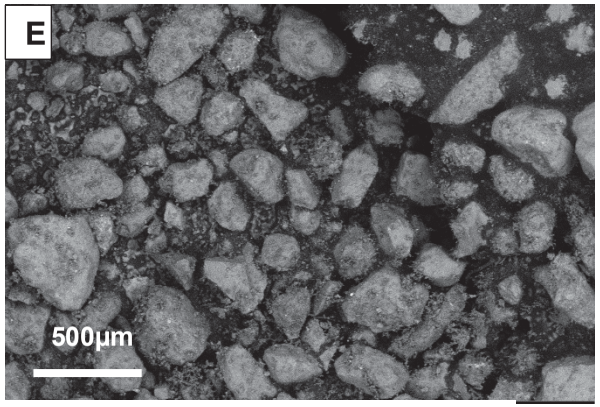
Bank 63µm-2mm January, 2011



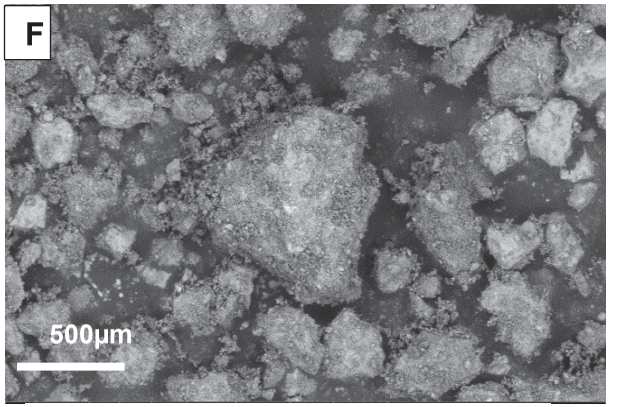
Suspended sediment January, 2011



Bed 63µm-2mm April, 2011



Bank 63µm-2mm April, 2011



Suspended sediment April 2011

Figure 6.2 The shape and arrangement of particles in 63µm-2mm bed and bank and in suspended sediment for the month of January 2011 and April 2011 (a) bed January 2011 (b) bank January 2011 (c) suspended sediment January 2011 (d) bed sediment April 2011 (e) bank sediment April 2011 (f) suspended sediment April 2011.

6.1.4 Sediment organic matter content by loss on ignition (LOI %)

The results for the organic matter content by loss on ignition (LOI) at 450^0C were compared for the bed, bank and suspended sediment for selected sediment samples (winter, spring, summer and autumn). The result indicated that a higher percentages of organic matter was associated with the suspended sediment and the <63µm particle fraction (Table 6.5).

Table 6.5 The average organic matter content determined by loss on ignition (±SD, n=2)

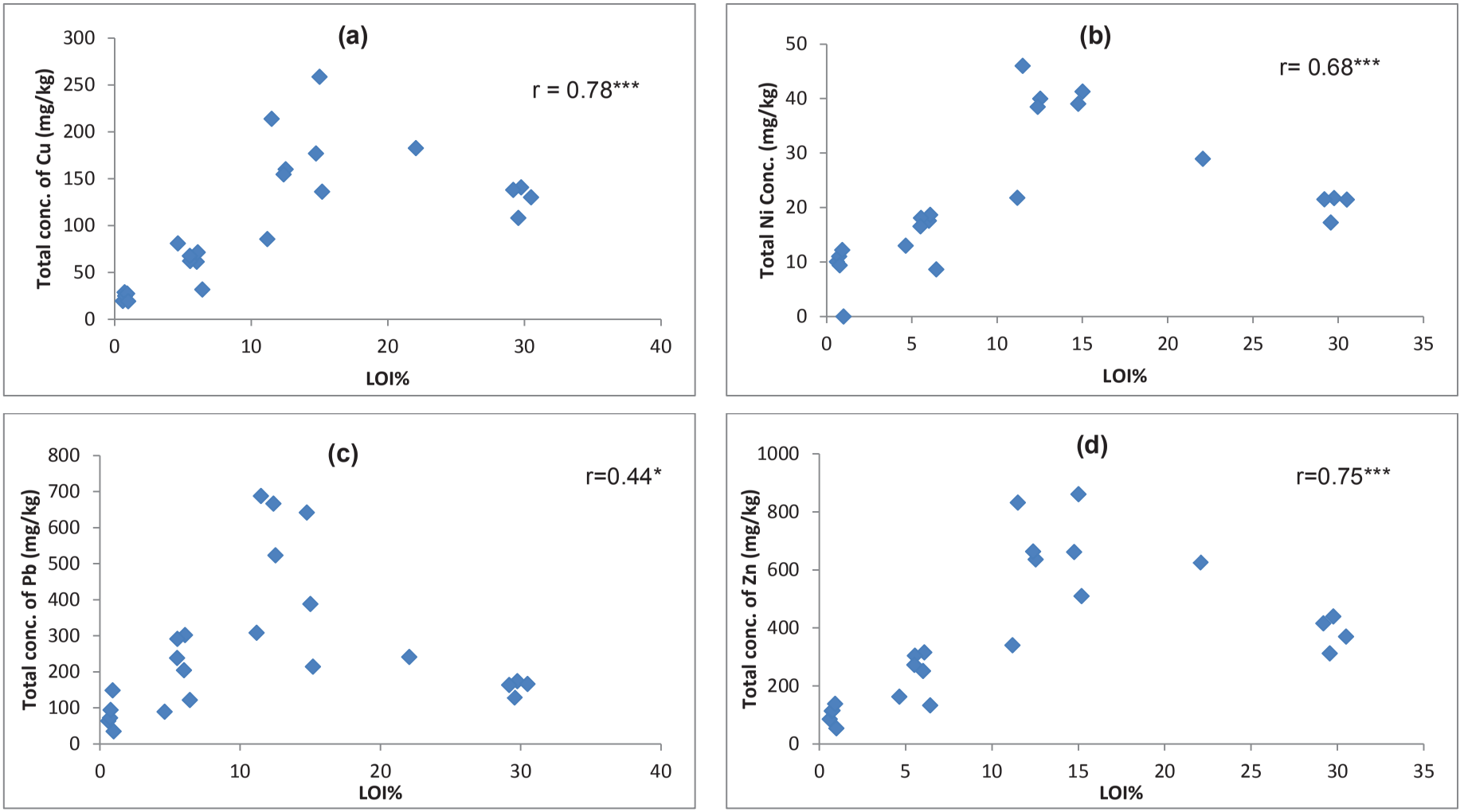
Season	Sample	Average LOI %
Winter (January)	Left monthly 1	22.07 ± 0.04
	Bed 63µm-2mm	0.61 ± 0.01
	Bank <63um	12.53 ± 0.21
	Bank 63µm-2mm	6.01 ± 0.13
Spring (April)	Left monthly 1	15.19 ± 0.30
	Bed 63µm-2mm	0.74 ± 0.03
	Bank <63um-April	14.76 ± 0.11
	Bank 2mm-April	6.09 ± 0.16
Summer (July)	Left monthly 1	15.01 ± 0.10
	Bed 63um-2mm	0.78 ± 0.00
	Bank <63um	12.38 ± 0.15
	Bank 63µm-2mm	5.54 ± 0.04
Autumn (October)	Bed 63µm-2mm	0.93 ± 0.01
	Bank <63um	11.5 ± 0.15
	Bank 63um-2mm	5.51 ± 0.29
Storm (May 2012)	Left after storm 1 May 2012	29.57 ± 0.30
	Left after storm 2 May 2012	29.77 ± 0.20
	Right after storm 1 May 2012	29.19 ± 0.57
	Right after storm 2 May 2012	30.51 ± 0.23
	Bed <63µm	4.64 ± 0.01
	Bed 63µm-2mm May 2012	1.00 ± 0.13
	Bank <63µm May 2012	11.19 ± 0.23
	Bank 63µm-2mm May 2012	6.43 ± 0.17

Note: There was insufficient mass of the <63µm in most bed sediment samples and in the Left monthly 1 (LM1) October samples for organic matter analysis

The suspended sediments contained the highest percentage of organic matter in all the given sampling months compared to the bed and bank sediment, ranging from 15% in the non-storm (January 2011, April 2011, July 2011 and October 2011) sample to 30% in the May, 2012 storm samples. The organic matter in the bank sediment was more than twice that retained in the bed sediment for the <63µm fraction, and about 6 times greater for the 63µm -2mm fraction. The bed sediment

retained the least organic matter, most especially in the 63µm - 2mm fraction which only consisted of about 1% organic matter. In general, the organic matter for the different sediment compartments followed the order: suspended sediment>bank>bed sediment. There was about a 7% to 10% increase in the percentage of organic matter contained in the suspended sediment during the May 2012 storm event compared to the non-storm samples. The organic matter content also increased slightly in the 63µm-2mm fraction of the bed and bank sediment during the May 2012 storm event (Table 6.5). There was no increase in organic matter content during the storm event for the <63µm bank sediment. In general, there was a significant negative correlation ($r=-0.67$, $p<0.001$) between the particles sizes (in all the sediment compartments combined for the months of January, April, July and October 2011) and the organic matter content (by loss on ignition).

Organic matter tends to increase binding sites for metal in sediment (Eggleton and Thomas, 2004; Charriau *et al.,* 2011). There was a significant positive relationship between the total concentration of metals (in the bed, bank and suspended sediment compartments) and with the organic matter (determined by loss on ignition) (Figure 6.3). The detailed results for the concentration of selected heavy metals in the bed, bank and suspended sediment are discussed in the next chapter (Chapter 7).



*p<0.05 ***p<0.001

Figure 6.3 The relationship between organic matter and heavy metal concentration in the bed, bank and suspended sediment (a) Cu (b) Ni (c) Pb (d) Zn.

6.1.5 Sediment chemical composition and mineralogy (X-ray diffraction)

Analysis of the mineral composition of Ravensbourne sediment using x-ray diffraction showed that the most common minerals present in the sediments were quartz [SiO_2], illite [$(KAl_2\ (Si_3Al)O_{10}(OH)_2$], muscovite [$K(Al.88FeO_{12})(Si_3Al)O_{10}(OH)_2$], calcite [$CaCO_3$], kaolinite [$Al_4(OH)_8(Si_4O_{10}$], dolomite [$CaMg(CO_3)_2$], montmorillonite [$(Al,Mg)_2Si_4O_{10}(OH)_2.4H_2O$] and goethite [(FeO(OH)] (Figures 6.4 - Figure 6.7).

Silicon oxide (quartz) had the highest peak (Figures 6.4 – Figure 6.7). A similar pattern of mineral distribution was found in each seasonal sample analysed (January, April, July and October in 2011) in all the sediment compartments. Figure 6.4 presents the mineral composition of the <63µm fraction for the bed and bank sediment. The mineral compositions of the larger fractions (63µm-2mm) of the bed and bank sediment are given in Figure 6.5. The mineral composition for suspended sediment is presented in Figure 6.6. Finally a comparison of the sediment compartment was shown for one sampling month – July 2011(Figure 6.7). The bed, bank and suspended sediment had a similar composition of minerals. The peak intensities for silicon oxide are prominent at 24^0, 30^0, 43^0, 47^0, 60^0 and 80^0 2Theta. Calcite is prominent at 34^0 2theta; muscovite was noticed at 4^0, 23^0 and 40^0 2theta, dolomite was recorded at 35^0 and 40^0 2theta angle, illite at 7^0 and 40^0 2theta, kaolinite at 13^0 and 28^0 2theta and finally, the peak for montmorillonite occurs at 3^0 2theta angle (Figures 6.4 – 6.7).

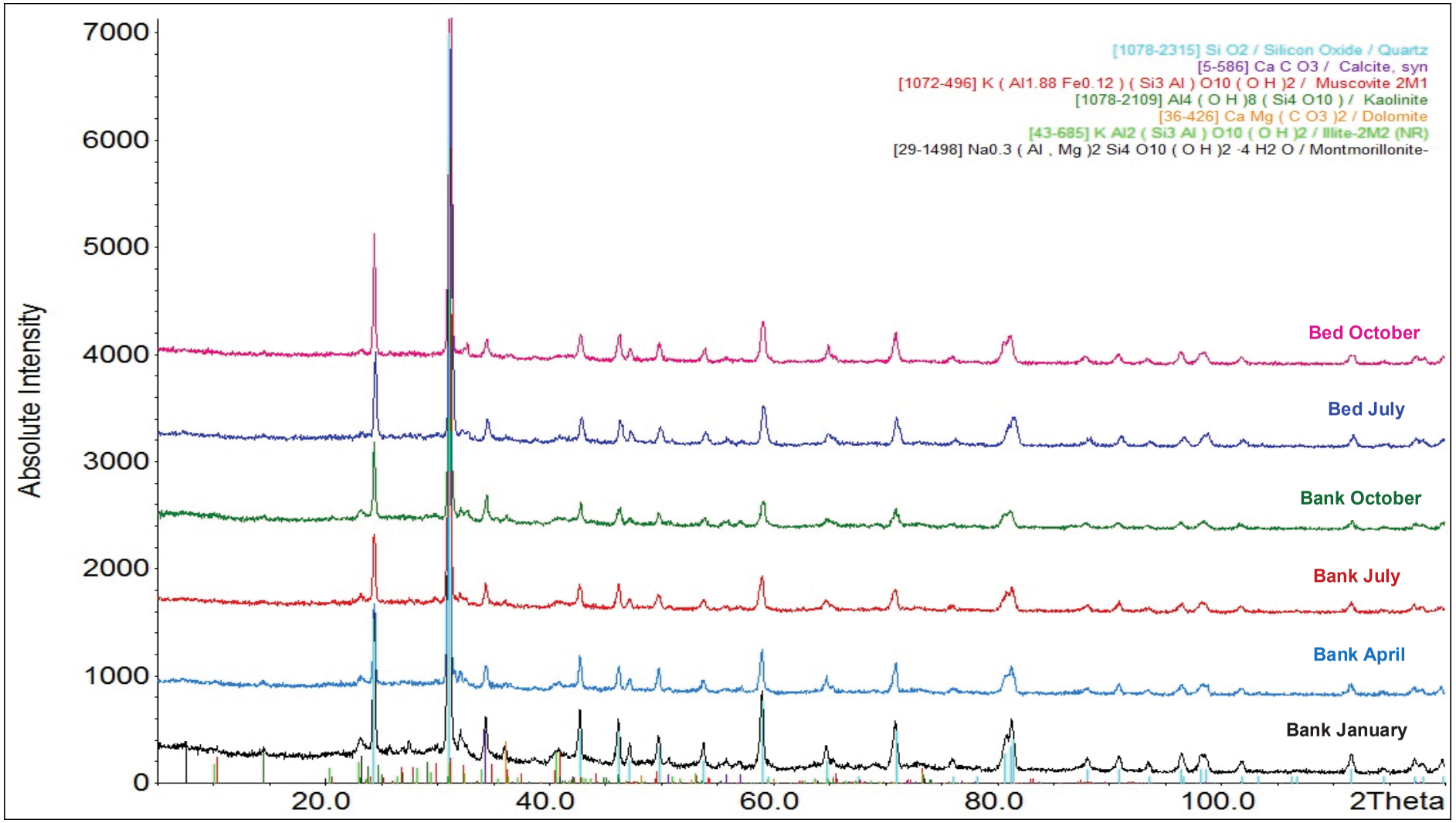


Figure 6.4 Mineral compositions by x-ray diffraction of the <63µm bed/ bank sediment for the month of January, April, July and October 2011. (**Note**: There were insufficient bed sediment samples for the <63µm fraction in the months of January and April)

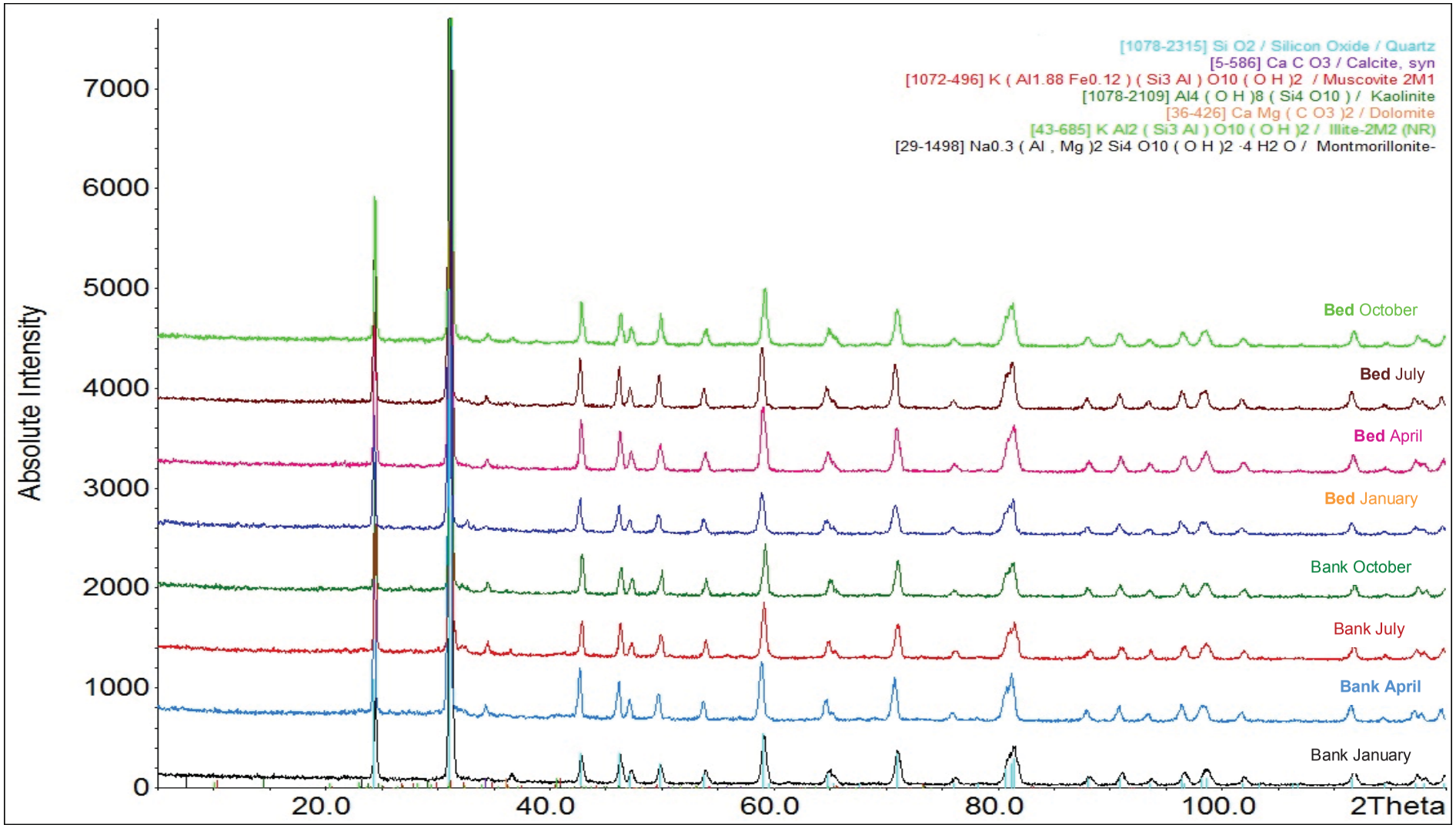


Figure 6.5 Mineral compositions by x-ray diffraction of the 63µm-2mm bed/bank sediment for the month of January, April, July and October 2011

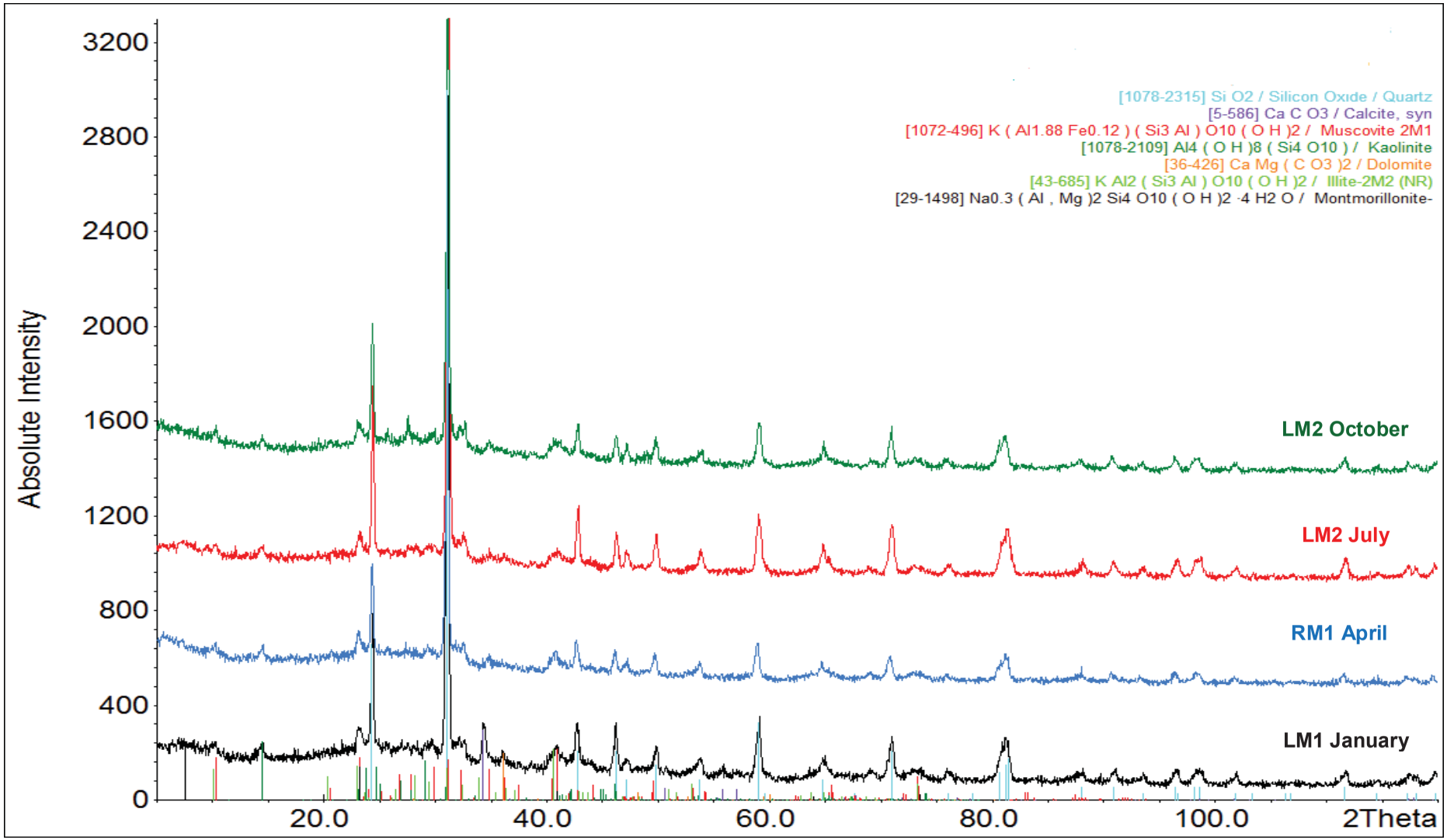


Figure 6.6 Mineral compositions by x-ray diffraction of the suspended sediment samples for the month of January, April, July and October 2011

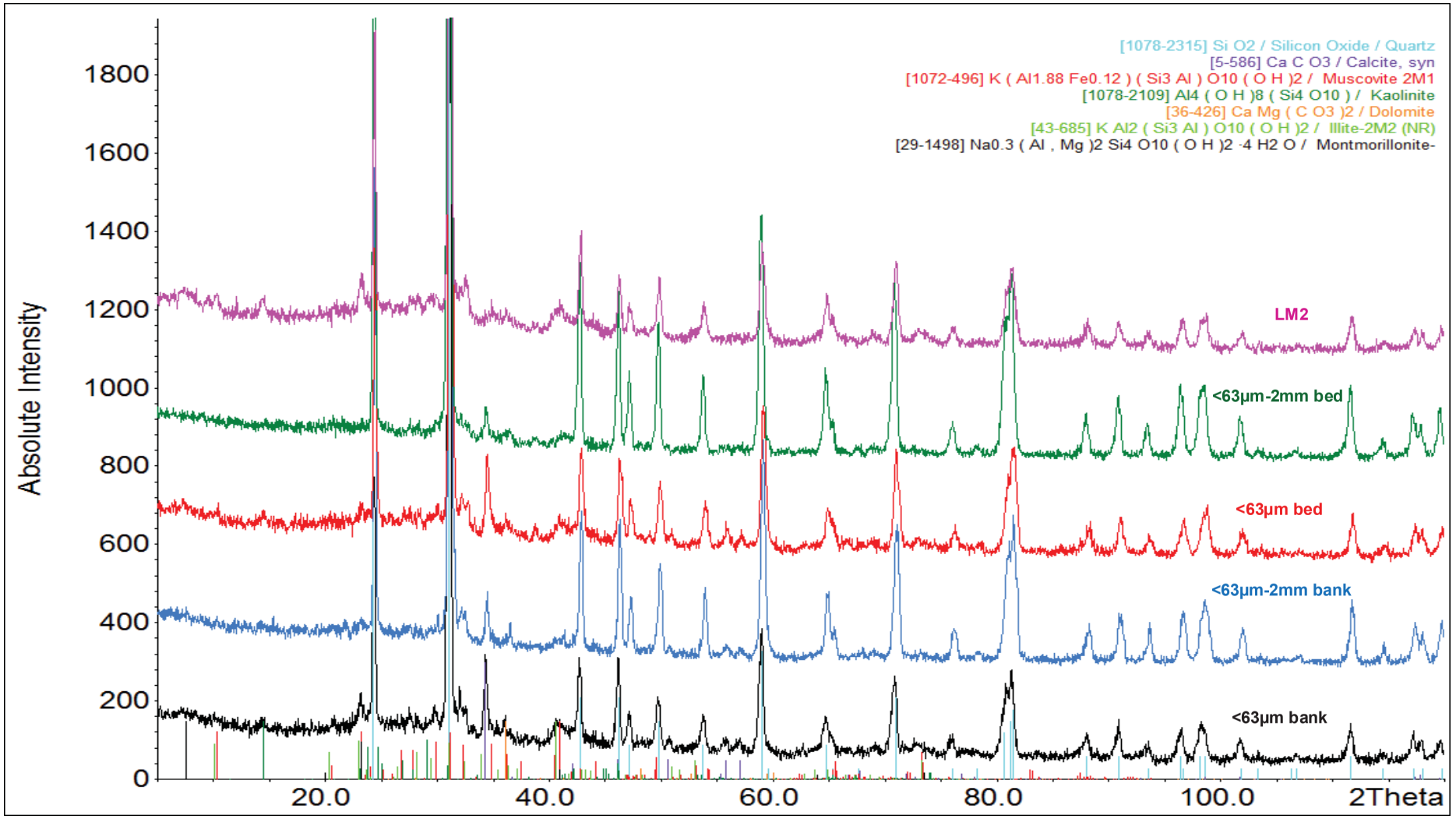


Figure 6.7 Mineral compositions by x-ray diffraction of the different compartment (bed, bank and suspended sediment) for the month of July 2011

A quantitative analysis for the mineralogy characteristics of sediment samples (July 2011 and the May 2012 storm sample) indicated that the dominant minerals were quartz, illite-smectite and muscovite (Table 6.6). These minerals constituted over 80% of the total mineralogy content for all samples. Higher quantities of quartz were associated with the 63µm-2mm fraction, particularly in the bed sediment.

Table 6.6 The percentage phase proportion of minerals in July 2011 and May 2012 (storm) samples

July 2011	Quartz, %	Illite-Smectite, %	Muscovite, %	Clinochlore, %	Calcite, %	Kaolinite, %	Dolomite, %	Goethite, %
Left monthly 1	21.28	61.99	10.38	3.10	0.61	4.45	0.47	0.23
Left monthly 2	20.56	56.14	10.65	3.18	1.26	6.06	1.91	0.24
Right monthly 1	21.74	63.35	8.49	1.58	0.63	3.02	0.95	0.24
Bed <63µm	48.13	39.22	4.75	1.42	4.48	1.35	0.43	0.21
Bed 63µm- 2mm	82.38	9.35	4.44	1.32	1.05	1.26	0.00	0.20
Bank <63µm	34.52	51.17	5.11	1.52	3.62	2.91	0.92	0.23
Bank 63µm- 2mm	67.66	25.45	0.93	1.39	2.76	1.33	0.25	0.21
May 2012 (storm sample)								
Left after storm1	21.02	68.89	3.27	1.63	1.93	1.55	0.98	0.73
Left after storm 2	19.83	70.27	3.29	1.63	1.94	1.56	0.98	0.49
Right after storm 1	13.42	71.32	3.34	3.32	3.28	1.58	2.99	0.75
Right after storm 2	13.50	69.81	3.36	3.34	4.62	1.59	3.01	0.76
Bed <63µm	41.11	36.59	13.26	2.83	2.23	2.69	0.85	0.43
Bed 63µm- 2mm	62.10	23.39	1.78	0.26	1.57	2.53	7.97	0.40
Bank <63µm	39.27	44.68	6.11	3.04	3.00	2.89	0.55	0.46
Bank 63µm- 2mm	68.39	20.23	1.77	2.64	1.25	2.52	3.18	0.00

The percentage of the rest of the minerals (kaolinite, calcite, muscovite and dolomite) varied between the sediment compartments (Table 6.6). The total percentage of muscovite obtained for the two sediment fractions (<63µm and 63µm – 2mm) of the bed sediment was greater than that obtained for the total muscovite in the <63µm and the 63µm – 2mm bank sediment (Table 6.6). The suspended sediment had the highest percentage of muscovite for the non-storm sample. A

similar pattern of mineral distribution in the non-storm samples were observed in the storm samples (May, 2012). The quantity of goethite was consistent (<0.3%) in the bed, bank and suspended sediment of the non-storm sample (July, 2011). The quantitative mineral characteristics also varied slightly between the storm and non-storm samples. Overall, there was more kaolinite mineral in the non-storm sample compared to the storm sample, and there was more dolomite in the storm sample compared to the non-storm sample. The non-storm sample follows the order for mineral characterization:

Illite-smectite>quartz>muscovite>kaolinite>calcite>clinochlore>dolomite>goethite

while the pattern for the storm samples follows the order:

Illite-smectite>quartz>muscovite>dolomite>calcite>clinochlore>kaolinite>geothite.

The major differences between the storm and the non-storm events are in concentration of dolomite and kaolinite. The sequestering abilities of clay minerals vary with the particular clay mineral due to the variations in their surface area and surface charge (Horowitz, 1991; He *et al.,* 2012). Kaolinite have a higher surface area and likely to sequester more heavy metals (Table 6.7). Horowitz (1991) gave the surface area of selected clay minerals, iron hydroxide and organic matters (Table 6.7).

Table 6.7 Surface area of selected clay minerals and for organic matter for sediment with diameters <2µm

Material	**Surface area (m2 g^{-1})**
Calcite	12.5
Dolomite	5.1[a]
Kaolinite	12 – 50
Illite	30 – 80
Montmorillonite (smectite)	50 – 150
Iron hydroxide	300
Organic Matter	1900

(Source: Horowitz, 1991)

a Brunauer- Emmett-Teller (BET) surface area of dolomite (Jame River Limestone)

Illite-smectite and quartz (silicon oxide) were the dominant minerals in all sediment compartments. Smectite minerals have large surface area (50 m^2g^{-1}-150m^2g^{-1}), and the binding abilities of clay minerals increase with increasing surface area.

6.2 Discussion

6.2.1 Sediment mass

The mass of <63µm sediment fraction collected in the bed sediment and the mass of suspended sediment collected in the suspended sediment were often insufficient for laboratory analysis. The concentration of contaminants in the suspended sediment is significant not only because it is a major source of food to benthic and pelagic organism, but also because it gives an indication of recent contaminants that are transported in rivers (Crane, 2003). However, sampling and analysis of suspended sediment are more of a challenge compared to the bed and bank sediment (Crane, 2003; Luoma and Rainbow, 2008), which also applies to the Ravensbourne River. This is significant as most sediment monitoring analysis are carried out using either the bed or suspended sediment (Devesa-Rey *et al.,* 2010; Huang and Wang, 2012; Sarma and Talukdar, 2009), which could present a challenge for sediment monitoring if sediment quality standards are to be based on the <63µm fraction or on the suspended sediment. Other methods of sampling suspended sediment such as continuous centrifugation can be used to obtain sufficient mass of suspended sediment (Hlavay *et al.,* 2004); however, it requires the use heavy field equipment and requires high operation costs (Long *et al.,* 2000; Schubert *et al.,* 2012). In rivers where the collection of the <63µm fraction presents is difficult because of gravel beds, the <2mm fraction could be sampled and this fraction used for sediment analysis. Certainly there are significant metal concentrations associated with this size fraction (Chapter 7).

The small quantity of sediment samples collected in the <63µm particle size in the bed and the suspended sediment samples does not necessarily imply a reduced risk of heavy metal contaminant exposure to aquatic and benthic organisms in the River Ravensbourne or rivers with similar gravel beds. The large surface area of the <63µm fractions means that it is likely to sequester heavy metal concentrations an order of magnitude higher than those retained in the larger fractions (63µm-2mm and the >2mm) (Salomons and Förstner, 1984), which may counterbalance the low proportions of this particle size in the sediment. It may be appropriate to develop EQS based on different sediment particle size for different river bed characteristics.

6.2.2 Particle size

Particle size is one the most important factors controlling the characteristics of sediment (Horowitz, 1991). The physical characteristics of sediment such as surface area and chemical characteristics such as mineral composition are highly dependent on sediment particle size (Förstner and Wittmann, 1981; Walling *et al*., 2003; Zhao *et al*., 2010). The particle size of suspended sediment can also affect the settling velocity, and the rate of deposition rate on the river bed (Horowitz and Elrick, 1987; Fox *et al.,* 2004). The sediment particle size collected in the bed, bank and suspended sediment varied with sampling period and sediment compartment. The suspended sediment consisted mainly of clay (<2μm) and silt (2μm-63μm) materials and would be expected to have low settling velocity (Fox *et al.,* 2004). As a consequence and metals associated with this suspended sediment fraction probably do not contribute substantially to the bed sediment metal concentration, simple because they tend to remain in suspension. The d50 of the suspended sediment ranged from 11.39μm to 77.46μm, which varied to a certain extent between each integrated suspended sediment tube samplers (Table 5.3). Overall, however, the d50 was predominantly below the <63μm particle size in all the integrated tube samplers. Similar results were published by Walling *et al.* (2000) for the Humber and Tweed catchment where more than 95% of fluvial suspended sediment particle size was <63μm. The average particle size (d50) of the suspended sediment was coarser than <63μm bank sediment in most of the monthly samples.

The particle sizes of the <63μm sediment fraction measured using the particle size analyser sometimes exceeded (>63μm) the sieved particle size (<63μm). This is mainly because sieving presents a partial method of measuring due to the imprecise measurement of irregularly shaped grain that are either rod or disk shaped that usually pass through the standard spherical aperture of the sieve mesh (Julien, 2010). Sieving also uses two dimensional technique in separating grain sizes, while the volume based technique used by the particle size analyser gives a three dimensional measurement of grain (Syvitski, 2007).

The <63μm fraction has been described as the most important fraction in the aquatic environment not only because higher concentrations of contaminants are often

associated with it, but also due to its ease of transportation in the aquatic environment, even during periods of low flow. The <63µm sediment fraction is also a major source of food for benthic organisms (Burden *et al.,* 2002; Luoma and Rainbow, 2008). However, a substantial amount of heavy metals contaminants is also associated with larger size particles that dominate the bed environment (Chapter 7). It might be unwise when setting environmental quality to standards to ignore the contaminant concentration of this sediment fraction; even though they may not be ingested by benthic organisms they provide a large part of the habitat for sediment dwelling organisms.

The differences in sedimentation rate which can vary from mm to 1-2cm per annum could be another reason for the variation in particle size composition in the bed and suspended sediment (Burden *et al*., 2002; Simpson *et al.,* 2005). The rate of overbank sedimentation rate is low for most British rivers and influenced by river geomorphology and flood events (Walling and He, 1994). This variation is significant for sediment monitoring especially if sediment environmental quality standards are to be based on a specific sediment size. For example, using the <63µm for sediment monitoring will favour monitoring of the bank sediment , because collecting sufficient sediment mass for laboratory analysis poses a challenge in gravel bed rivers with low sedimentation rates such as the Ravensbourne River. However, the bank sediment may not give representative samples of the river and may, therefore, not be appropriate to sample. Similarly, using the 63µm-2mm fraction for sediment monitoring will tend to omit the significant contribution of heavy metals from the <63µm fraction (Lin *et al.,* 2003). It is not clear what particle size has been used in setting most sediment guidelines (O'Connor, 2004), however the commonly used particle sizes reported in the literature for sediment analysis are the <63µm (Rodrigues and Formoso, 2006; Simpson *et al.,* 2011) and the <2mm (Karlsson *et al.,* 2010; Bartoli *et al.,* 2012) particle sizes. Perhaps the best option would be to delineate a fraction that incorporates both these i.e. from <63µm to 2mm, for analysis and setting standards.

The quantity of sediment transported in rivers increases during rainfall events and increased discharge (Aramaki *et al.,* 2010). The lack of relationship between the d50 of the suspended sediment and Ravensbourne River discharge could imply that

rainfall and discharge were not the major factors influencing particle size in the Ravensbourne. This has been reported by several authors in other rivers (Walling *et al,* 2000; Blanchard *et al.,* 2010). Walling *et al. (*2000) reported no relationship when the ultimate particle size was plotted against discharge in the Humber and Tweed catchment. A study carried out by Blanchard *et al.* (2010) in Dakota, United States indicated that only two out of the six sites investigated gave a significant relationship between the concentration of suspended sediment and river flow. The lack of significant relationship between suspended sediment and discharge have been attributed to the variation in sediment sources (land – use activities, flood events, topography) and flocculation (Blanchard *et al*., 2010). The transportation of coarser particle size increases with storm events (Lenzi and Marchi, 2000). In the Ravensbourne the storm event of May 2012 resulted in an increase in the average particle size for Left Monthly (1) suspended sediment and also appeared to be linked to an increase in the 63µm - 2mm particles in the bed sediment.

The morphology of the bed, bank and suspended sediment showed variation in morphology of the particle sizes and composition. All the sediment particles were irregularly shaped and not spherical in bed, bank and suspended sediment compartments. The bed sediment consists of large sizes which were deposited on river bed, while the smaller particles of the suspended sediment were transported in solution.

6.2.3 Organic matter

The ability of organic matter to sequester heavy metals in sediment is widely documented. Organic matter has a large surface area and substantially increases binding sites for metals in sediment (Luoma and Rainbow, 2008; Charriau *et al.,* 2011). The surface area of organic matter is higher than the surface areas of clay minerals and iron hydroxide (Horowitz, 1991; Luoma and Rainbow, 2008), indicating that organic matter plays a significant role in sediment quality and should be taken into consideration during sediment monitoring for any future environmental quality standards. The number of binding sites produced from organic matter is also dependent on the type of organic acid, for example fulvic organic materials have a larger binding surface compared to lignin (Luoma and Rainbow, 2008). The identification of the different types of organic matter is beyond the scope of this

study. The result from this study indicated that a higher percentage of organic matter was associated with the suspended sediment and the <63µm particle fraction. The suspended sediment contained a higher percentage of organic matter compared to the bed and bank sediment, and, therefore, was likely to retain more heavy metals (see chapter 7). However, in most sediment, the number of binding sites is not only influenced by organic matter content, but also the presence of iron oxides (Luoma and Rainbow, 2008). The role of organic matter in the chemical characteristics of sediment with increase in metal concentration is discussed in chapter 7.

6.2.4 Mineralogy

The Ravensborne bedrock consists of sedimentary rocks (London clay formation – silt and gravel) and alluvium superficial deposits which consist of clay, silt, sand and gravel. The sedimentary bedrock and alluvium deposits indicate that most of the clay minerals are detrital and can occur in abundance in any depositional environment (Weaver, 1956). Silicates, carbonates and clay minerals such as Illite, montmorillonite and kaolinite are the likely clay minerals found in any depositional environment (Weaver, 1956). Clay minerals play a significant role in the chemical characteristics of sediment due to their ability to sequester and trap heavy metals (He *et al.,* 2012). The mineralogy for the bed, bank and suspended sediments are similar, although different in proportion. It is probable that the sediment originated from the same source and that they are likely to have similar chemical characteristics in terms of heavy metal concentration already present in the minerals. The binding abilities of clay minerals differ with the particular clay mineral due to the variations in their surface areas and surface charges (Horowitz, 1991; He *et al.,* 2012). Illite-smectite and quartz (silicon oxide) were the dominant minerals in all sediment compartments in this study. The suspended sediment contained a high percentage of illite-smectite (39-71%), the bed sediment consisted mainly of quartz (41-82%) which is a non-reactive mineral (Wang and Jaffe, 2004), and the bank sediment contained (20-51%) of illite-smectite. Smectite minerals have large surface area (50 m^2g^{-1}-150m^2g^{-1}), and the binding abilities of clay minerals increase with increasing surface area. The heavy metal concentration in each of the sediment compartments is discussed in chapter 7.

Chapter 7

Sediment Total Heavy Metal Concentrations

7.0 Introduction

One of the objectives of this study was to compare determine if there are differences the concentration of heavy metals between different sediment compartments, that is, the bed, bank and suspended sediment. This chapter will describe the impact of sediment particle fraction (<63µm and 63µm–2mm), and sediment compartment on heavy metal concentration over a year's sampling period. The heavy metal concentrations in sediments are considered in the context of the UK Draft freshwater sediment quality guidelines.

7.1 The metal concentration in wet and dry sieved bed and bank sediment

Sieving, particularly wet sieving was applied in separating sediment grains in order to minimise the variation caused by the aggregation of sediment particles (Goossens, 2008). The results for the wet sieving and dry sieving showed variation in metal concentration with metal, and particle size (Figures 7.1 and 7.2). The Mann Whitney non-parametric test for the wet and dry sieved sediment for all the metals indicated that there were no significant difference ($p>0.05$) between the median concentration of heavy metals in the wet and dry sieved sediment of the bed and bank sediment for both sediment fractions (<63µm and the 63µm-2mm) (Table 7.1).

Table 7.1 Mann Whitney test for the sum of the heavy metal concentrations between the wet and dry sieved sediment

	<63µm bed	63µm-2mm bed	<63µm bank	63µm-2mm bank
Mann Whitney test P value	0.31	0.92	0.55	0.55

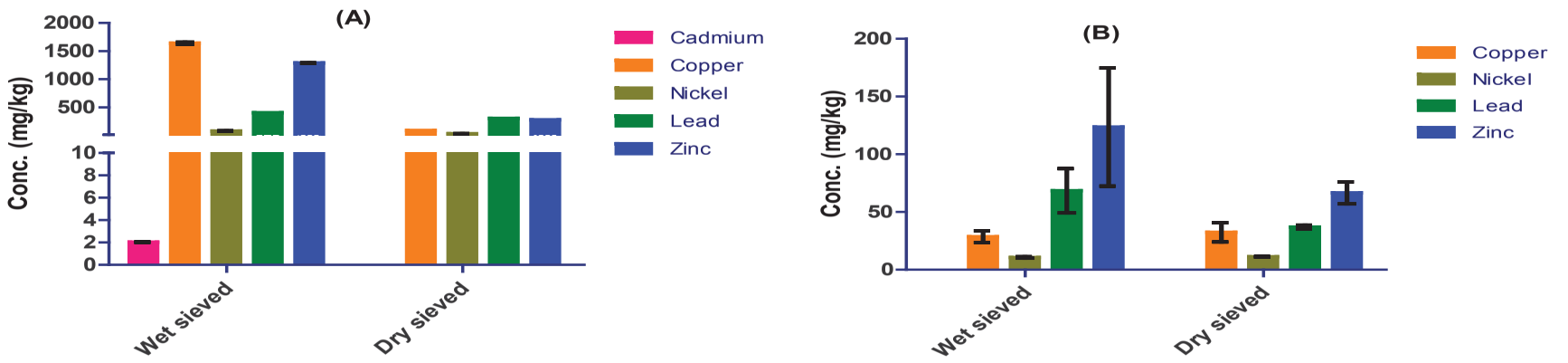


Figure 7.1 The concentration of heavy metals in wet and dry sieved <u>bed</u> sediment digested with aqua regia (a) <63µm fraction (b) 63µm-2mm fraction. The error bars represents the standard deviation of the mean of replicate analyses (n=3)

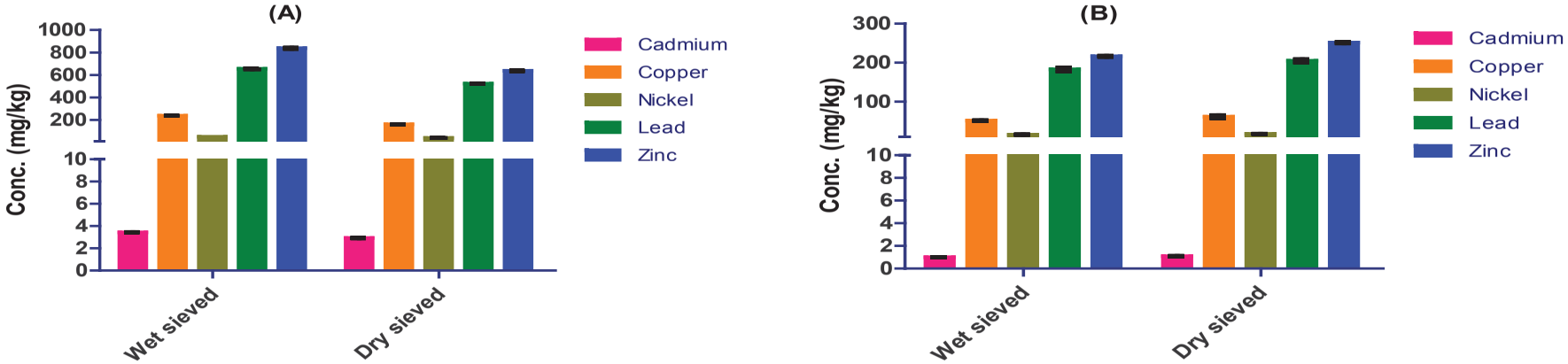


Figure 7.2 The concentration of heavy metals digested with aqua regia in wet and dry sieved <u>bank</u> sediment (a) <63µm fraction (b) 63µm-2mm fraction The error bars represents the standard deviation of the mean replicate analyses (n=3)

7.2 Sediment particle size and total metal concentration

The influence of different sediment particle sizes on sediment metal concentration was examined for the first sediment sample collected for this study (July, 2010) to determine how metal concentration varies with particle sizes and determine a suitable sediment particle size to use for the rest of the study. The bed and bank sediment samples of July, 2010 sieved into six different fractions (<63μm, 63μm-125μm, 125μm-250μm, 250μm-0.5mm, 0.5mm-1mm and 1mm-2mm) to investigate the effect of sediment particle size on heavy metal concentration. The results show that the concentration of metals in the different sediment fractions differed slightly from those commonly reported in literature. That is, the concentrations of metals increased with decreasing sediment particle size (Horowitz, 1991; Zhao *et al:* 2010). The concentrations of metals in the sediment particle sizes varied with metal and sediment compartment. The <63μm sediment fraction had the highest metal concentration for both the bed and bank sediment. There was a slight increase in the concentration of all the metals in the bank sediment for the 0.5mm-1mm and 1mm-2mm except for Ni (Figure 7.3). The concentration of copper in the <63μm bed sediment fraction was relatively high (1556.1mg/kg) compared to the concentration of copper in the <63μm bank sediment fraction (345.4mg/kg) (Figure 7.3b).

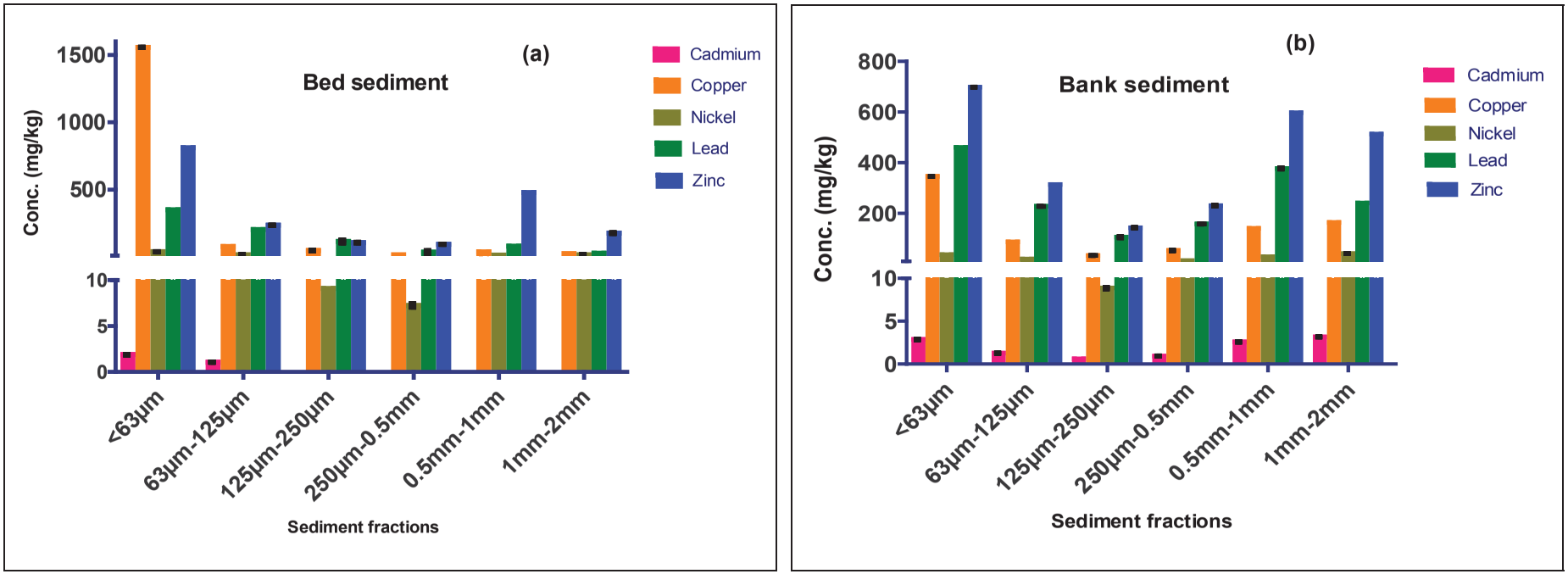


Figure 7.3 The mean concentration of the total heavy metals in different sediment fractions (a) bed sediment and (b) bank sediment for July, 2010 determined using aqua regia method. The bars represent the standard deviation of the mean of three replicates analyses (n=3).

Note: The maximum scale for metal concentration in the y axis was higher in the bed sediment (1,500 $mgkg^{-1}$) compared to the bank sediment (800$mgkg^{-1}$). The errors bars are not visible in samples where there was little or no standard deviation of the mean.

Zinc had the highest concentration of all the metals in each sediment fraction for both the bed and bank sediment except for the <63μm bed sediment. The cadmium concentration was lowest in both sediment compartments. Cadmium was mainly detected in the bank sediment and was below the limit of detention in most of the bed sediment fractions (Figure 7.3). The concentration of Cd was only detected in the <63μm and 63μm-125μm fraction of the bed sediment (Figure 7.3a), while Cd was present in all the bank sediment fractions (Figure 7.3b). In general, the sum of the metal concentrations associated with the >63μm fractions was larger than the <63μm fraction. The concentrations of all the heavy metals were also higher in the bank sediment compared to the bed sediment except for Cu, which is mainly due to the concentration of Cu in the <63μm bed sediment fraction.

7.3 Comparison of total heavy metal concentration in the bed, bank and suspended sediment compartments during the sampling period

One of the challenges associated with setting environmental quality standards for sediment is identifying the appropriate sediment compartment and sediment fraction to use (Crane, 2003). One of the aims for this study was to establish any differences in metal concentrations with sediment compartment and fraction that might have a significant consequence for selecting the appropriate compartment for sediment EQSs. The results showed that the concentrations of heavy metals varied with sediment compartment across the sampling months (Figures 7.4 – 7.6). In general, lead, zinc and copper were the dominant heavy metals in all the sediment compartments (Figures 7.4 -7.6). The concentrations of Cu, Pb and Zn were higher in bank sediment compared to the bed and suspended sediment. Ni and Cd had the lowest concentration in the bed, bank and suspended sediment compared to the other metals (Figures 7.4 -7.6).

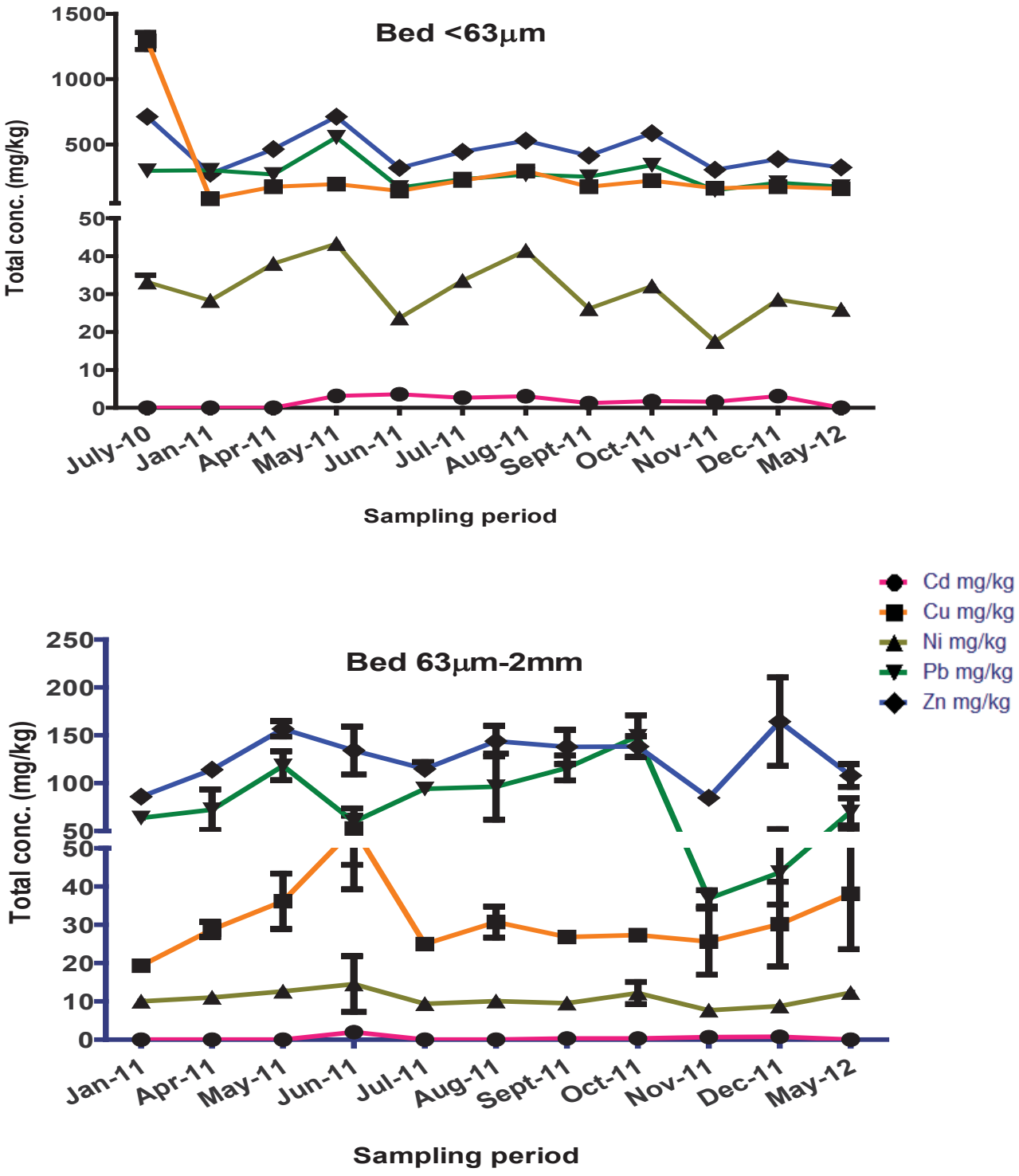


Figure 7.4 Total heavy metals concentration in bed sediment samples using aqua regia digestion (a) <63µm (b) 63µm-2mm. The bars represent the standard deviation of the mean of replicate analyses (n=3)

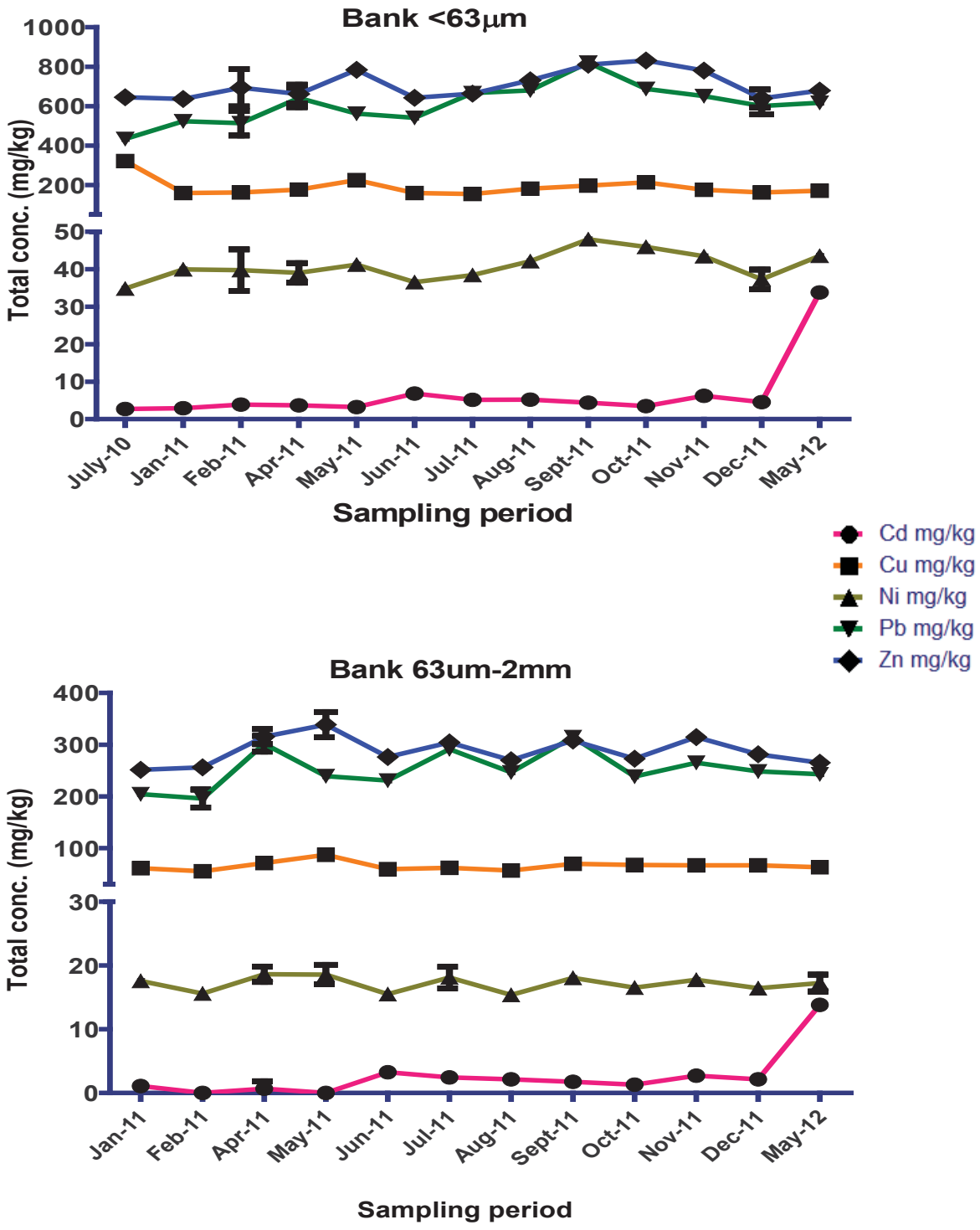


Figure 7.5 Total heavy metals concentration in bank sediment samples using aqua regia digestion (a) <63µm (b) 63µm-2mm. The bars represent the standard deviation of the mean of replicate analyses (n=3)

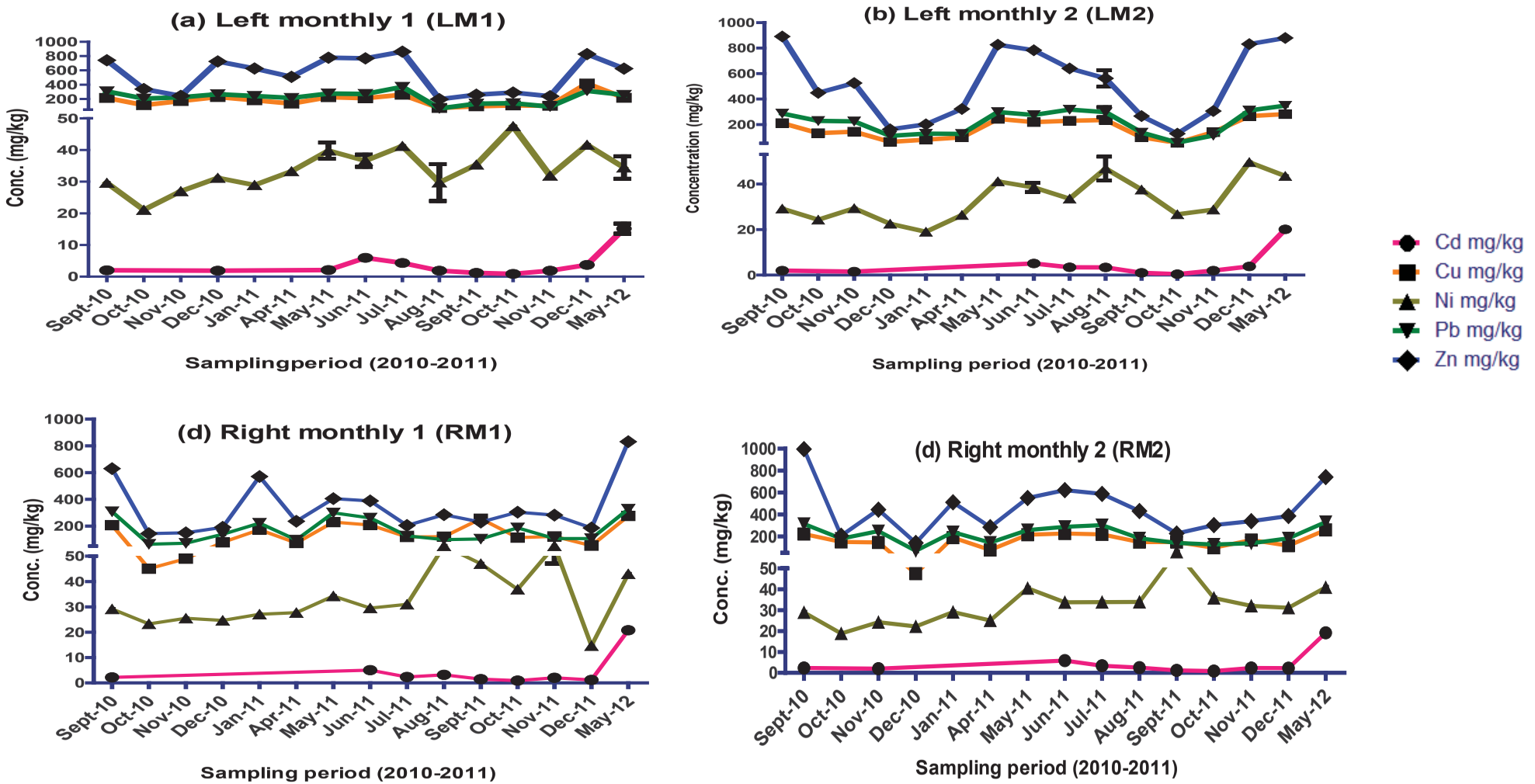


Figure 7.6 Total heavy metals concentration in suspended sediment samples using aqua regia digestion (a) Left monthly 1 (b) Left monthly 2 (c) Right monthly 1 (d) Right monthly. The bars represent the standard deviation of the mean of replicate analyses (n=3)

The integrated suspended tube samplers were sampled from September, 2010 - December, 2011, while the bed and bank sediment were sampled from January 2011-December, 2011. The bank sediment retained higher concentrations of all the heavy metals compared to the bed sediment and suspended sediment in most of the sampling months (Figure 7.4). The concentrations of metals varied with metal and sampling period for the bed and suspended sediment (Figure 7.5 and 7.6). The highest concentrations of heavy metals were associated with the <63µm fraction in both the bed and bank sediment. The <63µm sediment fraction had twice as much metals than the 63µm – 2mm fraction. This is quite different from the result obtained from the July, 2010 samples where the 0.5mm-1mm and 1mm-2mm contained almost as high concentration of metals as the <63µm. This is largely dependent on the proportion of each individual sediment fraction (63µm-125µm, 125µm-250µm, 250µm-0.5mm, 0.5mm-1mm and 1mm-2mm) present in the 63µm – 2mm fraction.

The Kruskal-Wallis test indicated that there was no significant difference between the metal concentration in the <63µm bed sediment and the suspended sediment, however there was significant difference ($p<0.05$) between the concentration of some of the metals in the suspended sediment and in the 63µm – 2mm bed sediment fraction (Table 7.2). The concentrations of metals in the <63µm bank sediment and the suspended sediment was only significantly different for the concentration of Pb and for Zn in Riight monthly suspended sediment (Table 7.2). There was no significant difference in total metal concentration between the 63µm-2mm bank sediment and the suspended sediment (Table 7.2). The concentration of metals between the bed and bank sediment also varied with metal and sediment fraction, there were no significant differences in the concentrations of all the metals for the <63um fraction bed and <63um fraction bank sediment, however, there was significant difference ($p<0.01$) for the 63µm- 2mm of the bed and in the 63µm- 2mm bank sediment for Pb, (Table 7.2). Variations in the concentration of metals across particle sizes (<63um and 63µm- 2mm) for the bed and bank sediment were significant and varied with metal (Table 7.2). Finally, the concentration of metals in each of the integrated tube samplers positioned differently along the river did not differ significantly ($p>0.05$) throughout the sampling period (Table 7.2).

Table 7.2 Kruskal-Wallis tests for the differences in the concentration of heavy metals between bed, bank and suspended sediment (n=10)

	Cd	Cu	Ni	Pb	Zn
LM1 vs LM2	NS	NS	NS	NS	NS
LM1 vs RM1	NS	NS	NS	NS	NS
LM1 vs RM2	NS	NS	NS	NS	NS
LM1 vs <63µm bed	NS	NS	NS	NS	NS
LM1 vs <63µm bank	NS	NS	NS	*	NS
LM2 vs RM1	NS	NS	NS	NS	NS
LM2 vs RM2	NS	NS	NS	NS	NS
LM2 vs <63µm bed	NS	NS	NS	NS	NS
LM2 vs <63µm bank	NS	NS	NS	*	NS
RM1 vs RM2	NS	NS	NS	NS	NS
RM1 vs <63µm bed	NS	NS	NS	NS	NS
RM1 vs <63µm bank	NS	NS	NS	***	**
RM2 vs <63µm bed	NS	NS	NS	NS	NS
RM2 vs <63µm bank	NS	NS	NS	**	NS
<63um bed vs <63µm bank	NS	NS	NS	NS	NS
LM1 vs bed 63µm- 2mm	**NS**	***	***	**NS**	***
LM1 vs bank 63µm- 2mm	**NS**	**NS**	*	**NS**	**NS**
LM2 vs bed 63µm- 2mm	*	***	***	**NS**	**
LM2 vs bank 63µm- 2mm	**NS**	**NS**	**NS**	**NS**	**NS**
RM1 vs bed 63µm- 2mm	**NS**	**	**	**NS**	**NS**
RM1 vs bank 63µm- 2mm	**NS**	**NS**	**NS**	**NS**	**NS**
RM2 vs bed 63µm- 2mm	**NS**	**	**	**NS**	**
RM2 vs bank 63µm- 2mm	**NS**	**NS**	**NS**	**NS**	**NS**
<63um bed vs bed 63µm- 2mm	**NS**	***	*	**	**
<63um bed vs bank 63µm- 2mm	**NS**	*	**NS**	**NS**	**NS**
bed 63µm- 2mm vs <63um bank	***	***	***	***	***
bed 63µm- 2mm vs bank 63µm- 2mm	**NS**	**NS**	**NS**	**	**NS**
<63um bank vs bank 63µm- 2mm	*	*	***	**NS**	**

* Significant at p<0.05, **significant at p<0.01, ***significant at p<0.001, NS-not significant
LM-Left monthly, **RM**-Right monthly

Note: Figures in **bold** are comparisons with the 63µm-2mm sediment fraction

7.4 Storm events

Storm event was defined in this research as rainfall greater than 30mm/day. The water column and bank sediment samples were the only samples collected for the February 2011 storm event due to an elevated river depth (>0.6m). The bed and suspended sediment were not collected for the February 2011 storm event due to health and safety reasons. The result for the May 2012 sediment analysis was used

to represent storm samples in this study for better comparison with the non-storm samples. The result for the May 2012 storm event showed an increase in most metal concentrations in all the suspended sediment samples over those present in non-storm event periods. The only exception to this was the Left monthly 1 suspended sediment which only showed an increase in the concentration of Cd (Figure 7.6). There was an increase in Cd concentration in the bank sediment for the May 2012 storm event (Figure 7.5). The bed sediment did not show any significant increase in metal concentration during storm the storm events (Figure 7.4).

The bank sediment was the only sediment sample collected for the Feb. 2011 storm event. A comparison of the metal concentration in the bank sediment collected for the Feb.2011 storm event and the bank sediment collected for the May 2012 storm event using the Mann Whitney non-parametric test showed that there were no significant difference ($p>0.05$) between each metal concentration in the <63um and 63um-2mm fractions (Table 7.3).

Table 7.3 Metal concentration in the bank sediment for the Feb.2011 and May 2012 storm events

	Bank sediment	**Cd, mg kg^{-1}**	**Cu, mg kg^{-1}**	**Ni, mg kg^{-1}**	**Pb, mg kg-1**	**Zn, mg kg-1**
Feb. 2011	<63um	3.87±0.44	162.69±21.99	39.76±5.56	513.76±62.38	693.88±94.58
	63um-2mm	0.00±0.00	55.29±2.67	15.57±0.42	196.03±17.40	256.11±5.57
May 2012	<63um	33.8±0.82	170.76±2.73	43.56±1.00	617.26±6.88	679.38±5.77
	63um-2mm	13.80±0.50	63.27±2.06	17.23±1.31	243.01±4.52	265.25±1.69

P=0.84 for the <63μm fraction, P=0.69 for the 63μm-2mm fraction

There was no significant relationship ($p>0.05$) between rainfall and the concentration of all the heavy metals in all the May 2012 storm sediment compartments except for Cd in one of the suspended sediment (LM1) sample and Cu in the right monthly 2 (RM2) suspended sediment sample (Table 7.4). The relationship between discharge and metal concentration in the May 2012 storm sediment was only significant for Cd in the 63μm -2mm fraction of the bed sediment (Table 7.5).

Table 7.4 Spearman correlation of heavy metals in sediment with rainfall

Spearman correlation with rainfall	Cd	Cu	Ni	Pb	Zn
Bed <63µm	0.52	-0.15	-0.14	-0.24	-0.41
Bed 63µm-2mm	0.16	0.21	0.13	-0.37	0.10
Bank <63µm	0.36	-0.58	-0.54	-0.58	-0.58
Bank 63µm-2mm	0.29	0.08	0.14	-0.14	0.08
Left monthly 1	**0.65***	0.25	-0.35	0.30	0.26
Left monthly 2	0.34	0.36	0.11	0.46	0.39
Right monthly 1	0.27	-0.04	-0.34	0.17	0.10
Right monthly 2	0.33	**0.55***	-0.25	0.53	0.45

***p<0.05**

Table 7.5 Spearman correlation of heavy metals in sediment with river discharge

Spearman correlation with discharge	Cd	Cu	Ni	Pb	Zn
Bed <63µm	0.41	-0.20	-0.33	-0.46	-0.09
Bed 63µm-2mm	**0.78***	0.48	-0.06	-0.45	0.23
Bank <63µm	0.30	0.10	-0.12	-0.01	0.08
Bank 63µm-2mm	0.47	0.40	0.02	0.04	0.48
Left monthly 1	0.16	0.02	0.14	0.05	0.11
Left monthly 2	0.24	0.31	0.25	0.15	0.45
Right monthly 1	0.18	-0.09	-0.14	0.03	-0.01
Right monthly 2	0.13	0.10	-0.10	-0.02	-0.03

***p<0.05**

7.5 The relationship between specific surface area (SSA), organic matter content (LOI %) and heavy metal concentration

The concentration of metal in sediment is known to be related to sediment particle size and surface area (See section 2.3, chapter 2). Metal concentration increases with decreasing surface area. In line with this a significant relationship was found between specific surface area and heavy metal concentration in the bed, bank and suspended sediment throughout the sampling period (Figure 7.7). The metals in the bed and bank sediment have a stronger significant positive correlation ($r>0.62$, $p<0.001$) with surface area compared to the suspended sediment (Table 7.6). The correlation of metals in the suspended sediment with SSA was significant in all the sediment compartments except for Cu and Ni (Table 7.6).

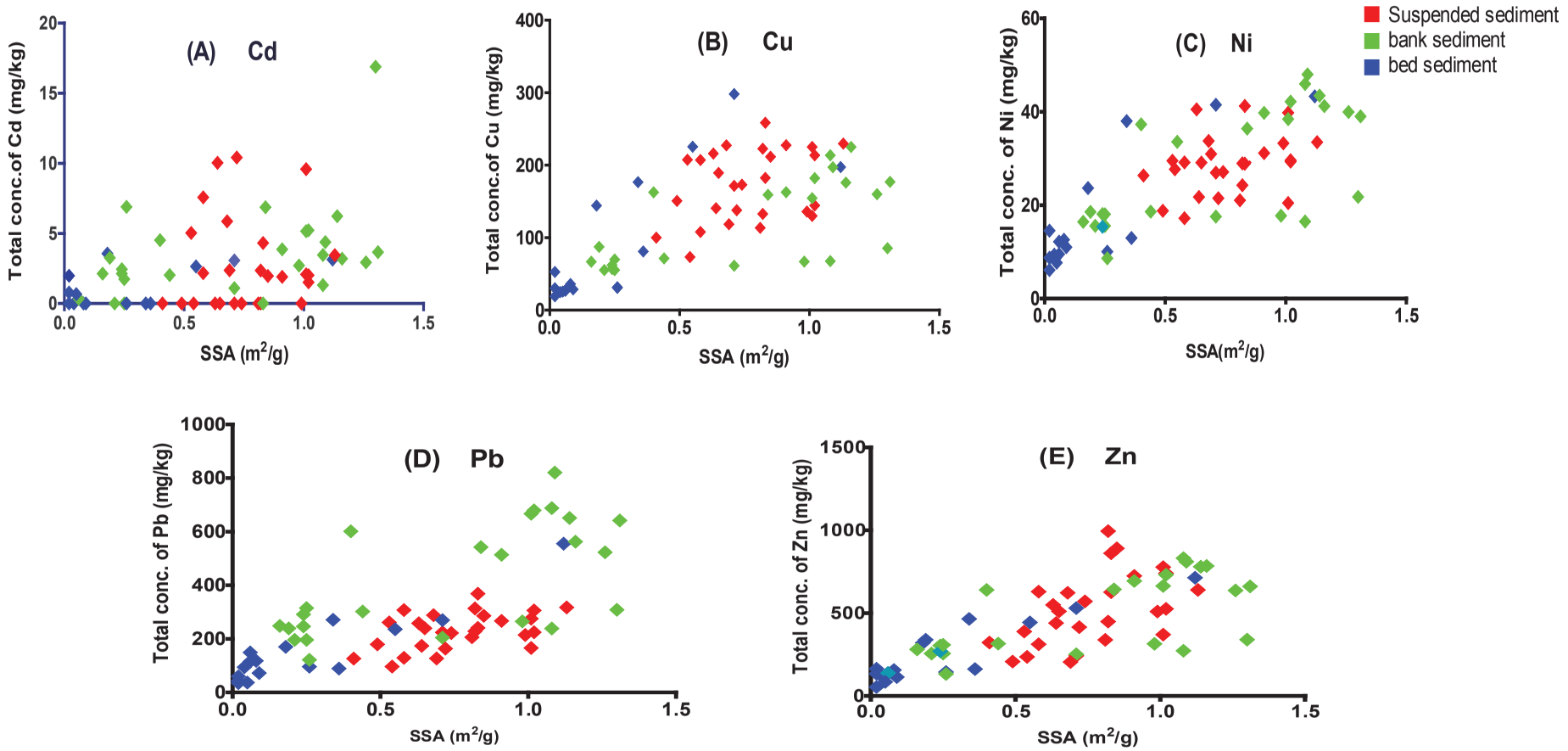


Figure 7.7 The relationship of sediment surface area (SSA) and heavy metal concentration in bed, bank and suspended sediment (n=67)

Table 7.6 Spearman correlation coefficient for the SSA of bed, bank and suspended sediment with each heavy metal (n=10)

	Cd	Cu	Ni	Pb	Zn
Suspended sediment(r)	0.10	0.37	0.35	0.43*	0.58**
Bed sediment (r)	0.24	0.79***	0.79***	0.79***	0.76***
Bank sediment (r)	0.46*	0.68***	0.70***	0.62***	0.64***

*** p<0.001, **p<0.01, *p<0.05

There were no significant relationship between the organic matter content (LOI %) and metal concentration in the bed and suspended sediment except for Zn in the suspended sediment (Table 7.7). However, the concentration of metal increases with organic matter content in the bank sediment, and the relationship was significant (Table 7.7).

Table 7.7 Spearman correlation coefficient for the organic matter content (LOI %) of bed, bank and suspended sediment with each heavy metal

LOI%	Cu	Ni	Pb	Zn
Bed sediment (n=6)	0.26	0.26	0.14	0.43
Bank sediment (n=10)	0.76*	0.78*	0.73*	0.73*
Suspended sediment (n=7)	-0.57	-0.71	-0.68	-0.79*

*p<0.05

7.6 The heavy metal concentration in sediment and the UK Draft freshwater sediment quality guidelines

The draft UK sediment quality guidelines are intended to protect aquatic life (Hudson-Edwards *et al.,* 2008). Sediment quality is assessed based on the threshold effect level (TEL) and the predicted effect level (PEL) (Table 7.8). The threshold effect level is the minimum concentration below which adverse effects occur rarely, while the predicted effect level is the concentration above which adverse effects are expected to occur frequently (Swartz, 1999; Hudson-Edwards *et al.,* 2008). The draft sediment quality guidelines for England and Wales for the selected metal are given below (Table 7.8).

Table 7.8 Draft freshwater sediment quality guidelines for England and Wales for Cd, Cu, Ni, Pb and Zn.

Heavy metals	UK TEL[a] ($mgkg^{-1}$)	UK PEL[b] ($mgkg^{-1}$)
Cd	0.596	3.53
Cu	36.70	197.00
Ni	18.00	35.90
Pb	35.00	91.30
Zn	123.00	315.00

(Source: Hudson-Edwards *et al*., 2008)

a TEL: Threshold effect level; draft freshwater sediment quality guidelines.
b PEL: Predicted effect level; draft freshwater sediment quality guidelines

The concentration of heavy metals in the bed, bank and suspended sediments of the Ravensbourne in comparison with the draft UK sediment quality guidelines were studied using boxplots. The median concentrations of all the heavy metals in the bed, bank and suspended sediment from January 2011 – December 2011 were used for the comparison (Figures 7.8 -7.12).

The compliance of metals with the draft sediment quality guidelines (TEL and PEL) varied with metal and with sediment compartment (Figures 7.8 - 7.12).

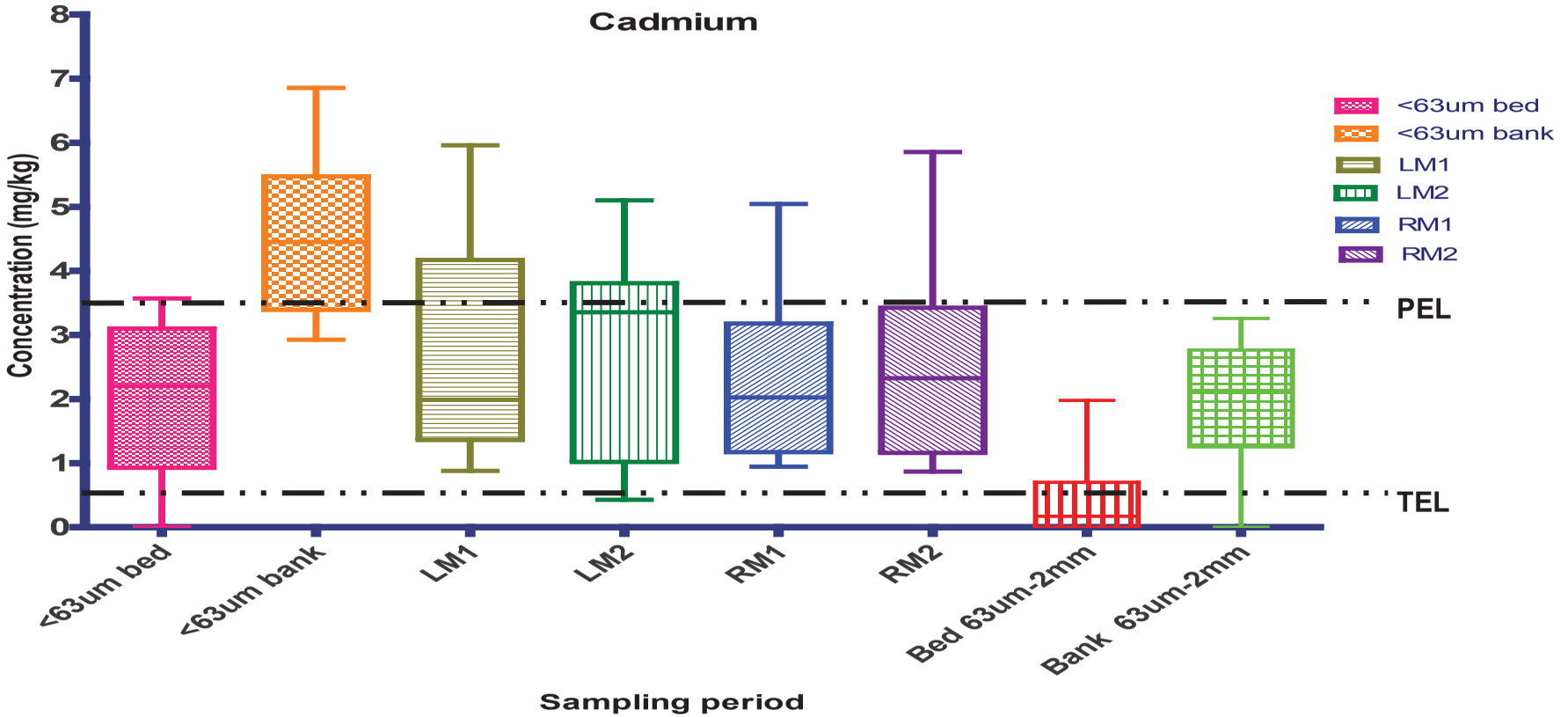


Figure 7.8 The concentration of Cd in bed, bank and suspended sediment (Jan. –Dec. 2011) compared to the threshold effect level (TEL) and predicted effect level (PEL) of the UK draft freshwater sediment quality guidelines

The horizontal lines within the boxplots represent the median concentration of heavy metals for each sediment compartment throughout the sampling period (January-December, 2011). The whiskers represent the minimum and maximum concentration, and the top and base of the box represent the upper and lower quartile. The horizontal dashed line running across the figure represents the UK draft threshold effect level (TEL) and the predicted effect level (PEL)

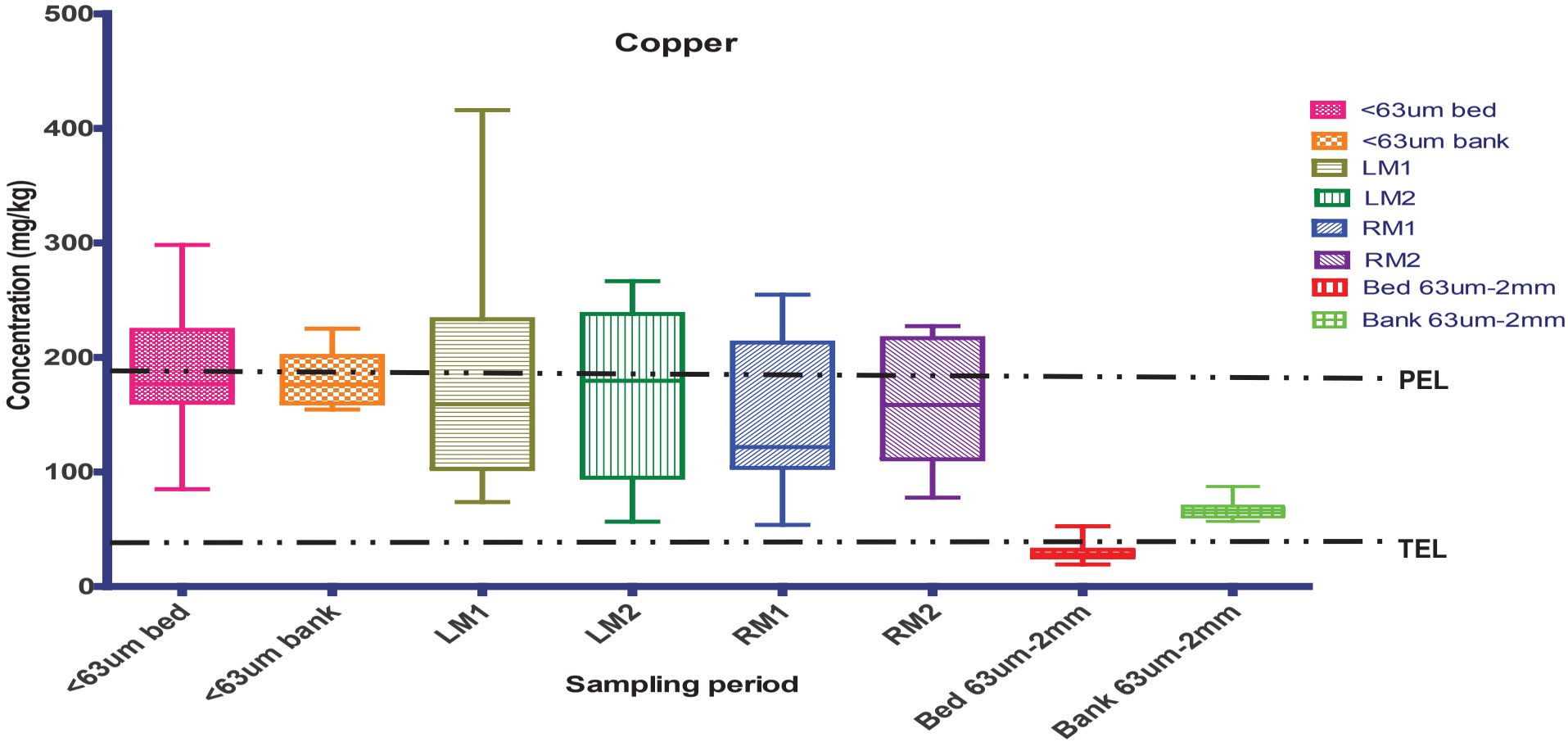


Figure 7.9 The concentration of Cu in bed, bank and suspended sediment (Jan. –Dec. 2011) compared to the threshold effect level (TEL) and predicted effect level (PEL) of the UK draft freshwater sediment quality guidelines

The horizontal lines within the boxplots represent the median concentration of heavy metals for each sediment compartment throughout the sampling period (January-December, 2011). The whiskers represent the minimum and maximum concentration, and the top and base of the box represent the upper and lower quartile. The horizontal dashed line running across the figure represents the UK draft threshold effect level (TEL) and the predicted effect level (PEL)

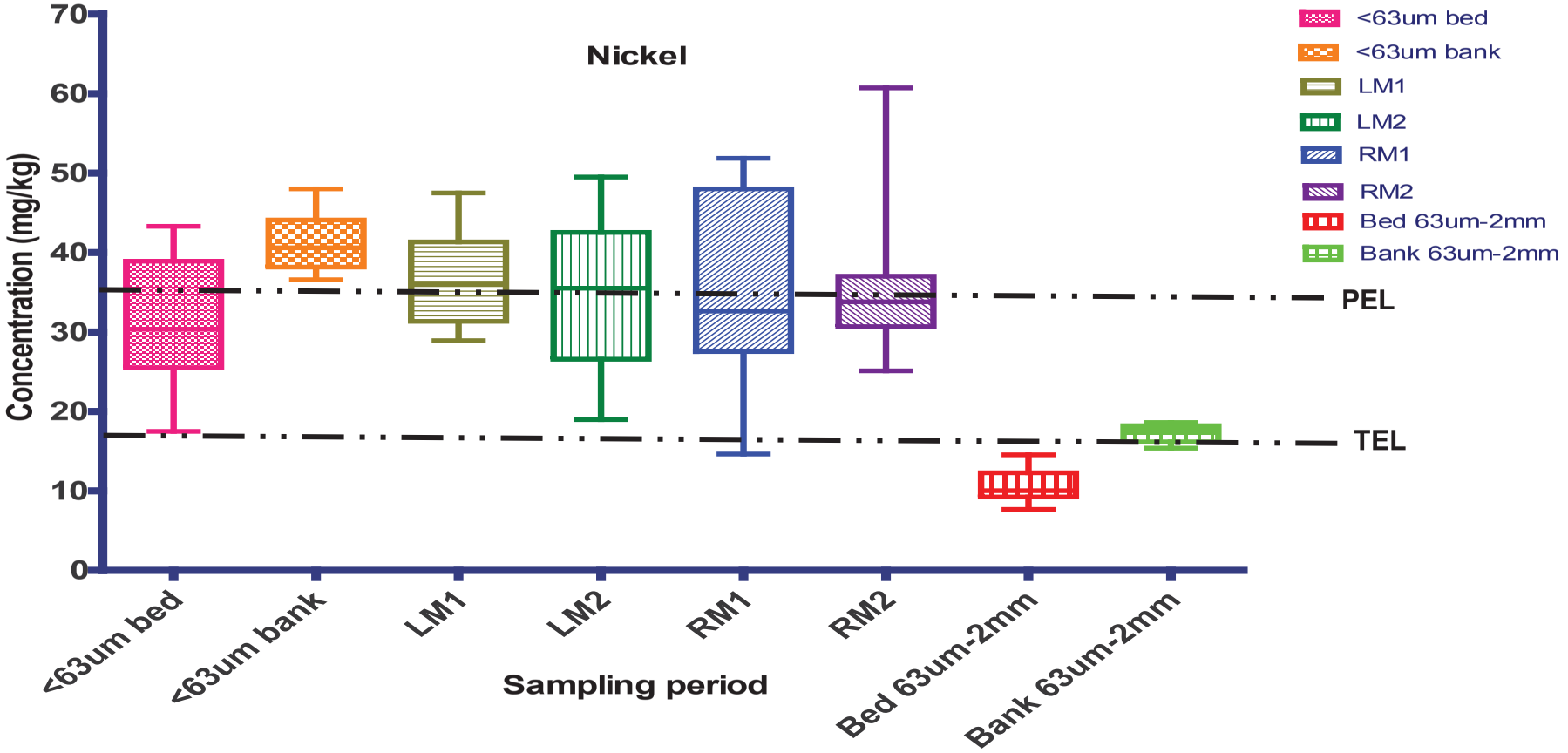


Figure 7.10 The concentration of Ni in bed, bank and suspended sediment (Jan. –Dec. 2011) compared the threshold effect level (TEL) and predicted effect level (PEL) of the UK draft freshwater sediment quality guidelines

The horizontal lines within the boxplots represent the median concentration of heavy metals for each sediment compartment throughout the sampling period (January-December, 2011). The whiskers represent the minimum and maximum concentration, and the top and base of the box represent the upper and lower quartile. The horizontal dashed line running across the figure represents the UK draft threshold effect level (TEL) and the predicted effect level (PEL)

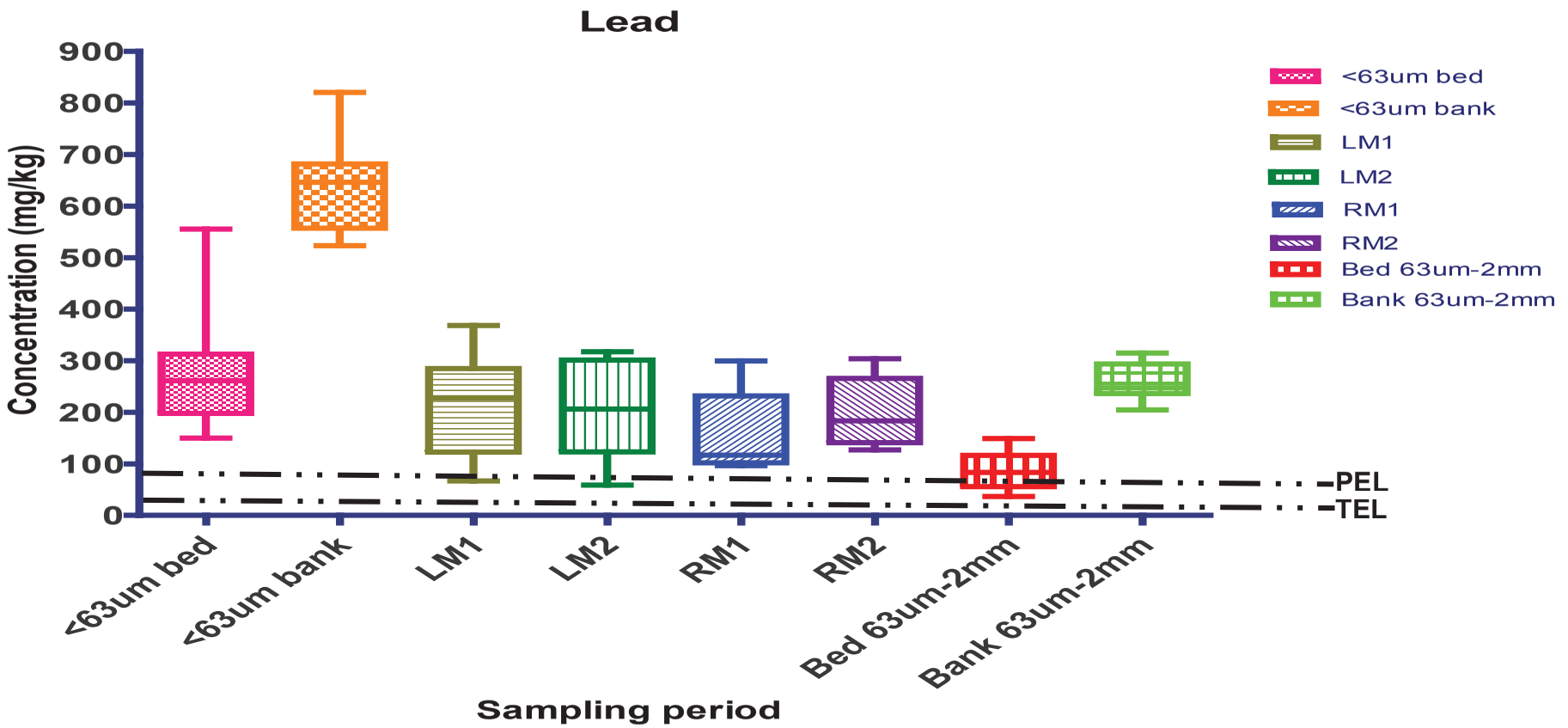


Figure 7.11 The concentration of Pb in bed, bank and suspended sediment (Jan. –Dec. 2011) compared to the threshold effect level (TEL) and predicted effect level (PEL) of the UK draft freshwater sediment quality guidelines

The horizontal lines within the boxplots represent the median concentration of heavy metals for each sediment compartment throughout the sampling period (January-December, 2011). The whiskers represent the minimum and maximum concentration, and the top and base of the box represent the upper and lower quartile. The horizontal dashed line running across the figure represents the UK draft threshold effect level (TEL) and the predicted effect level (PEL)

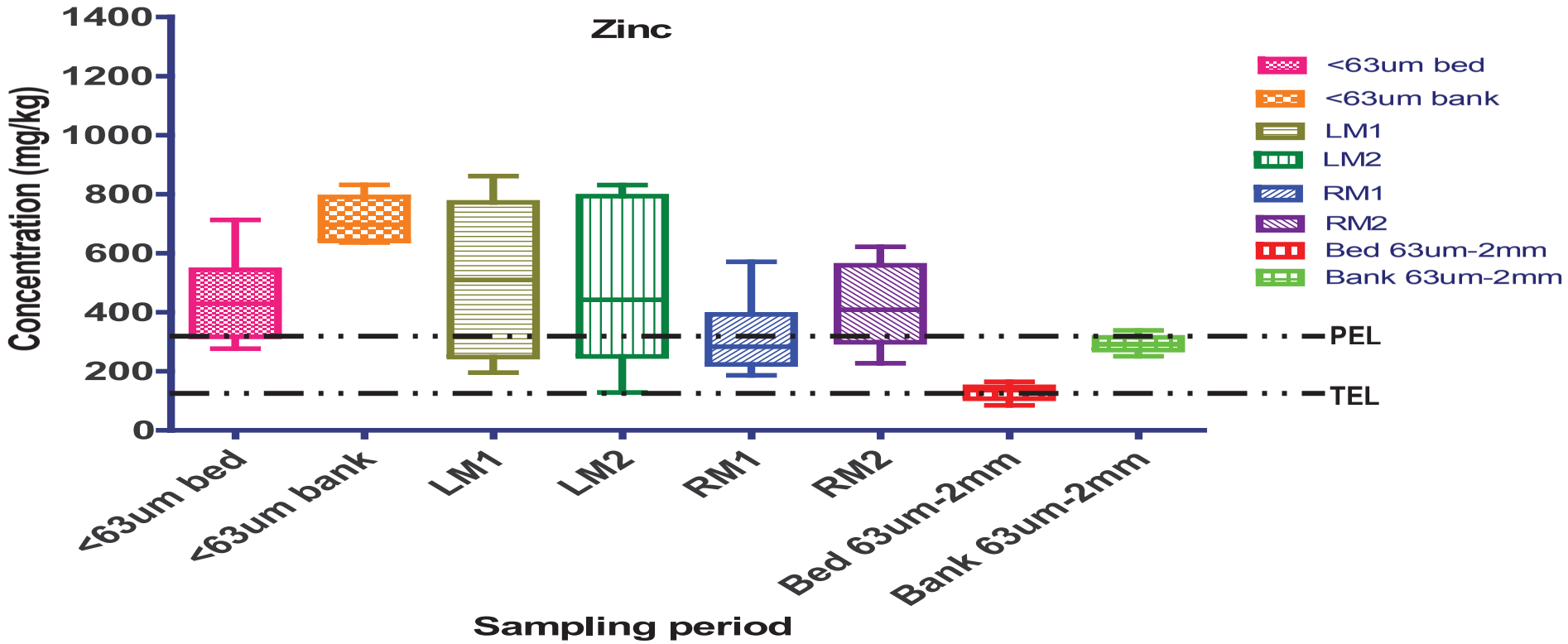


Figure 7.12 The concentration of Zn in bed, bank and suspended sediment (Jan. –Dec. 2011) compared to the threshold effect level (TEL) and predicted effect level (PEL) of the UK draft freshwater sediment quality guidelines

The horizontal lines within the boxplots represent the median concentration of heavy metals for each sediment compartment throughout the sampling period (January-December, 2011). The whiskers represent the minimum and maximum concentration, and the top and base of the box represent the upper and lower quartile. The horizontal dashed line running across the figure represents the UK draft threshold effect level (TEL) and the predicted effect level (PEL)

The concentration of metals in the bed, bank and suspended sediment consistently exceeded the draft UK TEL sediment guideline except for Cd and Zn in the 63µm - 2mm bed sediment. However, the metals concentrations in each sediment compartment were mainly below the UK PEL guideline except for Pb and Zn (Figures 7.11 and 7.12).

A comparison of the metal concentrations in the Ravensbourne sediment with the TEL sediment quality guidelines from other countries showed that the metal concentrations in the Ravensbourne exceeded the TEL sediment guidelines (Table 7.9). Similarly, a comparison of the Ravensbourne results with the PEL sediment guidelines from other countries showed that the sediment quality objective (SQO) Netherland Intervention was the only guideline that the metal concentrations in the sediment complied with, and even then with the exception of Pb (Table 7.10).

Table 7.9 Comparison of the annual average metal concentration in Ravensbourne sediment with threshold effect sediment quality (TEL) guidelines (mg kg^{-1})

Sediment Quality Guidelines	Cd	Cu	Pb	Ni	Zn
UK Draft predicted effect level (PEL)	0.6	35.7	35	18	123
Threshold effect level (TEL) Canada	0.6	35.7	35	18	123
Effects range low (ERL) Ontario	5	70	35	30	120
Lowest effect level (Florida) (LEL)	0.6	16	31	16	120
Consensus based -Threshold effect concentration (CBTEC)	0.99	31.6	35.8	22.7	121
Australian and New Zealand Environment and Conservation Council Effects range low (ANZECC ERL)	1.2	34	47	21	200
Sediment Quality Objective Target (SQO) Netherlands	0.8	36	85	35	140
Interim Sediment Quality Guidelines Hong Kong ISQG-low	1.5	65	75	40	200
Reference Value (Flanders RV)	1	20	0.1	28	168
Left monthly suspended sediment (AA)[a]	**3**	**181**	**211**	**37**	**535**
<63µm Bed sediment (AA)[a]	**2**	**187**	**276**	**31**	**444**
<63µm bank sediment (AA)[a]	**5**	**179**	**626**	**41**	**716**

a indicates annual average (n=10) **Figures in bold represent Ravensbourne sediment**

Table 7.10 Comparison of the annual average metal concentration in Ravensbourne sediment with Extreme effect sediment quality (also PEL) guidelines (mg kg^{-1})

Sediment Quality Guidelines	Cd	Cu	Pb	Ni	Zn
UK Draft sediment quality guidelines (PEL)	3.53	197	91.3	35.9	315
Toxic effect threshold (TET) Canada	3	86	170	61	540
Consensus based probable effect concentration (CB PEC)	4.98	149	128	48.6	459
SQO Netherland Intervention	12	190	530	-	720
Reference Value (RV) Flanders	6	126	0.8	174	1057
Extreme Elevated Stream Sediments Illinois	20	200	100	-	300
Australian and New Zealand Environment and Conservation Council (ANZECC)	10	270	220	52	410
Left monthly suspended sediment (AA)[a]	**3**	**181**	**211**	**37**	**535**
<63µm Bed sediment (AA)[a]	**2**	**187**	**276**	**31**	**444**
<63µm bank sediment (AA)[a]	**5**	**179**	**626**	**41**	**716**

a indicates annual average (n=10) Figures in bold represent Ravensbourne sediment

Note: The draft UK PEL sediment quality guidelines is the same as the Canadian midrange effect sediment quality guides

7.7 The relationship between the concentrations of heavy metal in sediment compartments to that in the overlying water column

The concentration of all the heavy metals in the bed, bank and suspended sediment were a magnitude higher than the concentration in the water column (Figure 7.13). Increases and decreases in the metal concentration in the sediment compartments were not reflected by similar changes in the metal concentration in the water column (Figure 7.13). In fact apart from the rise in metal concentration in May and June 2011, which was probably due to point source pollution (see section 5.1, chapter 5), the water metal concentration varied little.

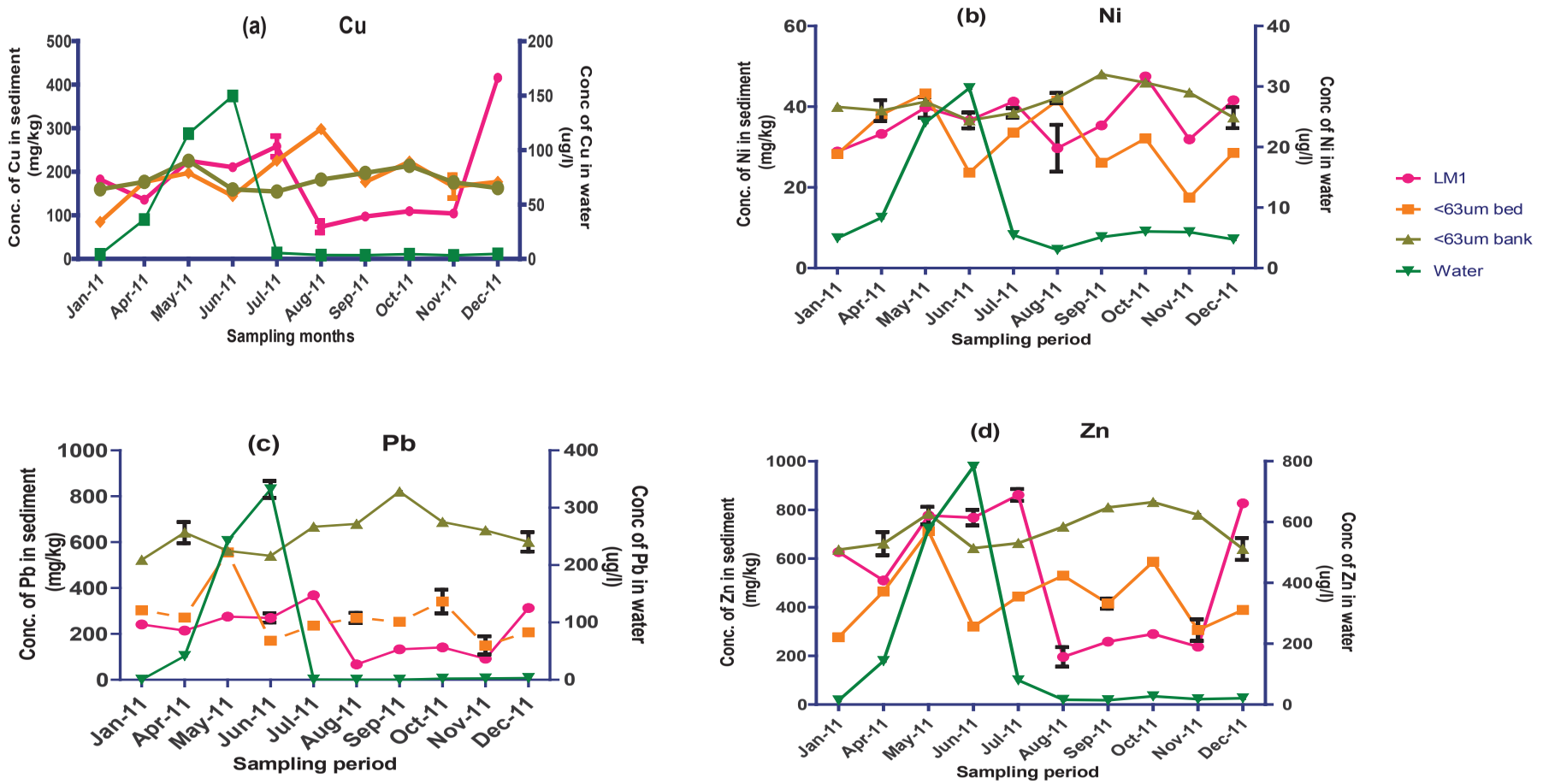


Figure 7.13 Comparison of metal concentration in bed, bank and suspended sediment against the concentration in water column. The error bars represent the standard deviation (n=3) of the mean of three replicate analysis (a) Cu (b)Ni (c) Pb (d) Zn. LM1 stands for left monthly.

Note: The left monthly integrated suspended sampler (LM1) was used to represent the suspended sediment compartment and the small fraction (<63μm) was used to represent the bed and bank sediment, and the concentration of water was expressed in μg/l in order to compare metal concentrations.

There was no significant correlation between the heavy metals concentration in sediment (<63µm bed, <63µm bank and suspended sediment) and the metal concentration in water except for Cu, Pb and Zn in Left monthly 1 suspended tube sampler (Table 7.11).

Table 7.11 The Spearman correlation of heavy metals in the sediment (suspended sediment, <63µm bed and <63µm bank) and the water column (n=10 of samples)

	LM1	<63µm bed	<63µm bank
Cd	0.71	0.52	-0.07
Cu	**0.69***	-0.02	-0.18
Ni	0.43	-0.37	-0.72
Pb	**0.71***	-0.19	-0.53
Zn	**0.71***	0.30	-0.30

***P<0.05**

7.8 Variations total metal extraction techniques

A comparison of total metal extraction for different sediment fractions was made using HF/$HClO_3$ /HNO_3 and aqua regia (1$HN0_3$:3HCl) (Figure 7.14 – 7.18). There were no significant differences in the concentration of metal extracted using either the HF/$HClO_3$ /HNO_3 or aqua regia in the sum of the <63µm, 63µm - 125µm, 125µm - 250µm, 250µm -500µm, 500µm-1mm and 1mm – 2mm fractions for both the bed and bank sediment (Table 7.12).

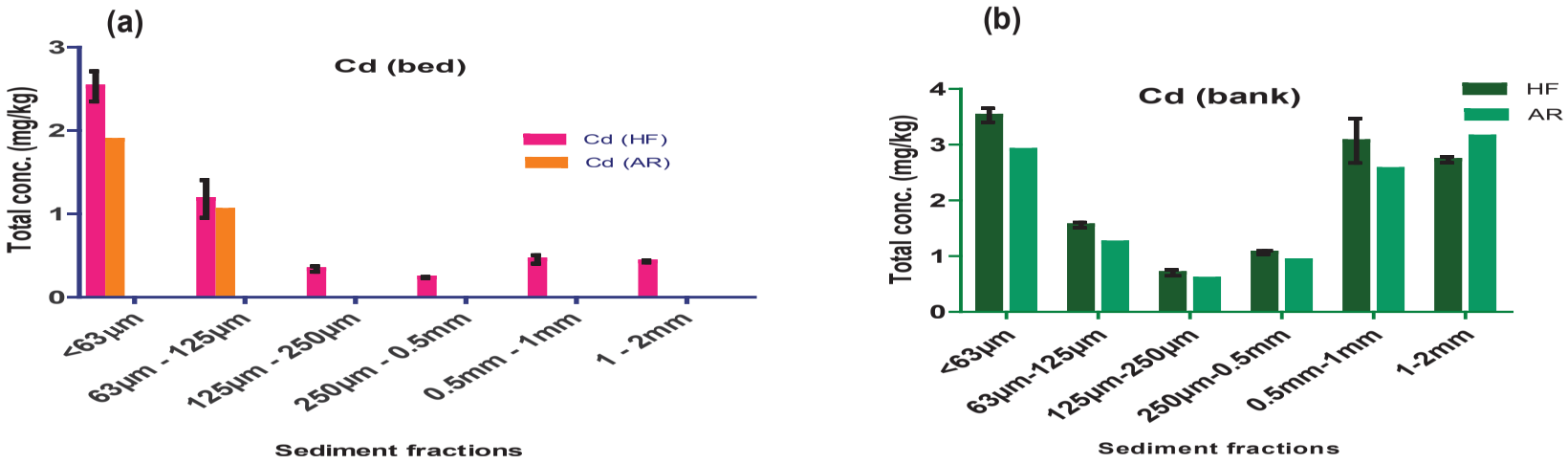


Figure 7.14 The concentration of Cd in different sediment fractions using $HF/HClO_3$ /HNO_3 and aqua regia (a) bed sediment (b) bank sediment. The error bars represents the standard deviation of the mean (n=3)

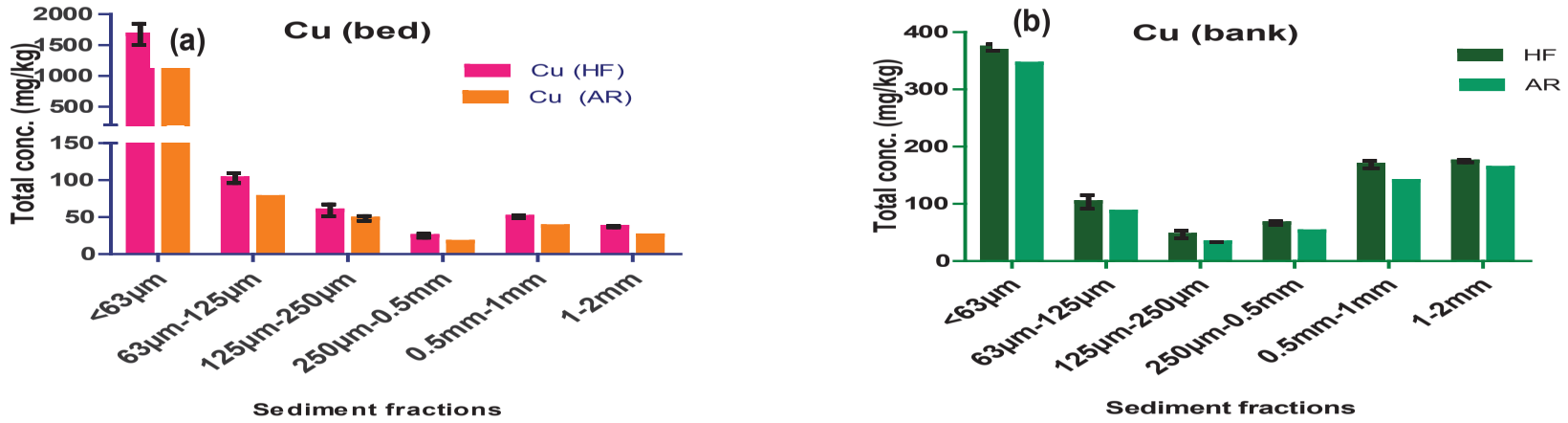


Figure 7.15 The concentration of Cu in different sediment fractions using $HF/HClO_3$ /HNO_3 and aqua regia (a) bed sediment (b) bank sediment. The error bars represents the standard deviation of the mean (n=3)

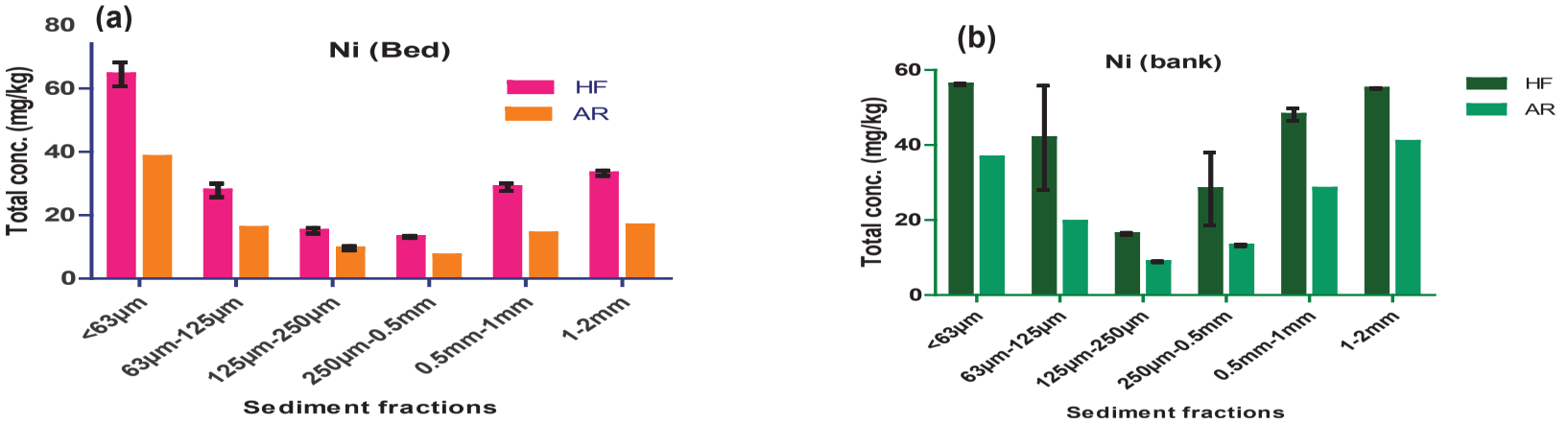


Figure 7.16 The concentration of Ni in different sediment fractions using HF/$HClO_3$ /HNO_3 and aqua regia (a) bed sediment (b) bank sediment. The error bars represents the standard deviation of the mean (n=3)

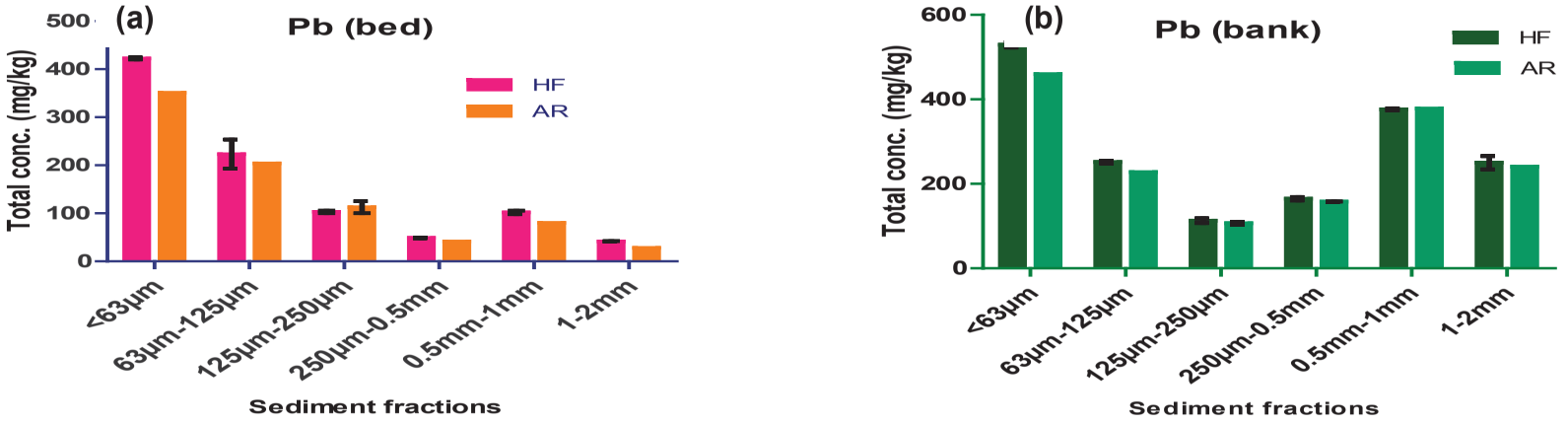


Figure 7.17 The concentration of Pb in different sediment fractions using HF/$HClO_3$ /HNO_3 and aqua regia (a) bed sediment (b) bank sediment. The error bars represents the standard deviation of the mean (n=3)

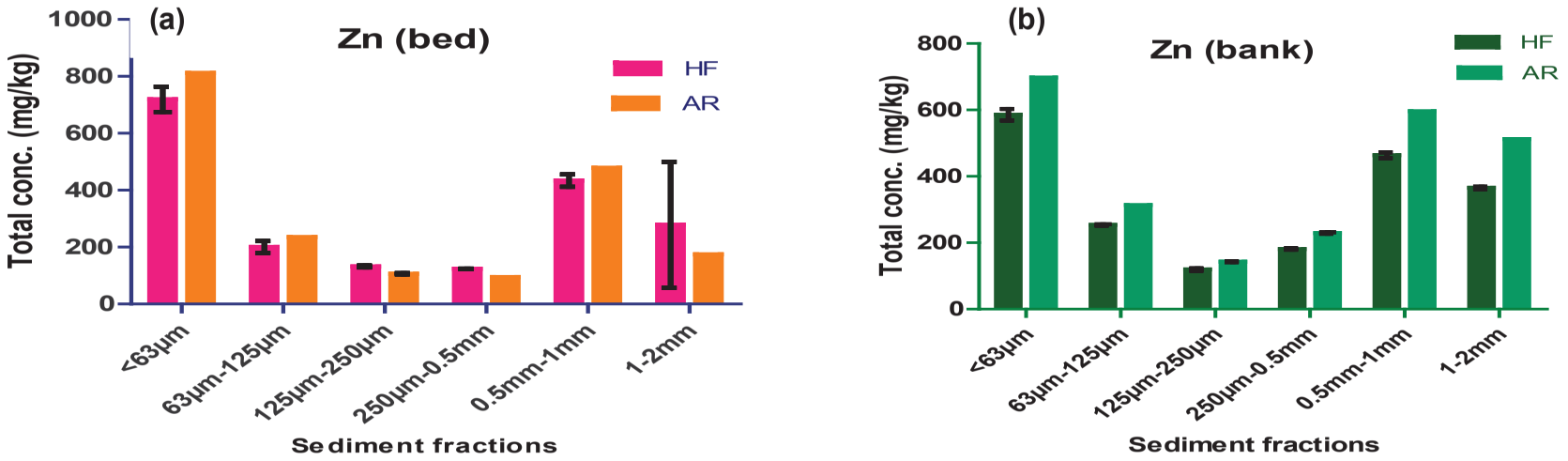


Figure 7.18 The concentration of Zn in different sediment fractions using HF/$HClO_3$ /HNO_3 and aqua regia (a) bed sediment (b) bank sediment. The error bars represents the standard deviation of the mean (n=3)

Table 7.12 Mann Whitney test of statistical difference between the HF/$HClO_3$ /HNO_3 and aqua regia extracting solution

Mann Whitney test	Bed[a]	Bank[a]
Cd	b	p>0.05
Cu	p>0.05	p>0.05
Ni	p>0.05	p>0.05
Pb	p>0.05	p>0.05
Zn	p>0.05	p>0.05

(a) Using the sum of all the different sediment fractions

(b) Insufficient data for analysis

7.9 Discussions

7.9.1 The metal concentration in wet and dry sieved bed and bank sediment

Sieving is the most commonly used method for separating sediment into different particle sizes (Simpson *et al.,* 2005); although sieving is reported to possibly change the physical characteristics of the sediment (Barlett and James, 1980; Simpson *et al*., 2005). The result of wet sieving or dry sieving of sediment indicated that the method used does not necessarily have a significant effect on the concentration of metals in sediment (Table 7.1). Wet sieving with the water from the river is often recommended as a way of preserving sample integrity and a more efficient sieving method for separating finer fractions, particularly the <63μm and 63μm –150μm, with a 63% higher recovery than dry sieving (Soares *et al*., 1999; Simpson *et al.,* 2005; Luoma and Rainbow, 2008). However, this study indicated that there is no significant difference in the metal concentration measured for the bed and bank sediment irrespective of whether it was wet sieved or dry sieved. It appears that a representative sample of each fraction was obtained from using both methods of sieving.

7.9.2 The effect of particle sizes on metal concentration

Sediment particle size is the most significant factor that affects sediment's ability to sequester and transport heavy metals, and a major reason for the heterogeneity in the chemical characteristics of sediment in the aquatic environment (Horowitz and Elrick, 1988; Burden *et al.,* 2002). The impact of the grain size on heavy metal concentration for six different sediment particle sizes in this study indicated that the highest concentration of each metal was associated with the <63μm fraction. High concentrations of each metal, however, were also associated with the 0.5mm -1mm and 1mm-2mm sediment fraction (Figure 7.3). This is slightly different from the usual trend of increasing metal concentrations with decreasing particle size often reported in literature (Singh *et al*., 1999; Zhao *et al.,* 2010). However similar results of the large sediment fractions retaining high concentrations of metals have also been reported by Lin *et al*. (2003), Zafra *et al*. (2011) and Kayhanian *et al,* (2012). High concentrations of heavy metals associated with large sediment fractions have been attributed to the agglomeration of smaller size fractions to form a coarse fraction (Parizanganeh, 2008); binding of fine grain fractions to the surface of larger particles

(Burden *et al.,* 2002); the presence of large detrital grain (particles from pre-existing rock) (Moore *et al.,* 1989) and sources of metals being associated with the large sediment fractions (Salomons and Forstner, 1984; Zafra *et al.,* 2011). The increases in binding sites created by high organic matter content and Fe/Mn content in larger fractions have also been suggested as important (Moore *et al*., 1989; Lin *et al*., 2003), this is also likely to be the case for the Ravensbourne River due to high metal concentration associated with the bank sediment and the bank sediment had the significant relationship with organic matter content (Table 7.7). An increase in the contact /residence time between large fractions and metals in the aquatic environment due to low transport rate may also be a significant influence as well (Singh *et al*., 1999). The Ravensbourne have low discharge (Table 5.1, section 5.1) for most of the sampling period, and an increase in the contact/residence is likely to be a contributing factor in the high concentration of metals in the large sediment fractions (Figure 7.3).

The bank sediment retaining higher concentrations of all the metals could possibly be a reflection of the variability in grain size and specific surface area in the bed and bank sediment. The SSA of the bank sediment was consistently higher than that of the bed sediment in both the <63µm and 63µm-2mm sediment fractions throughout the sampling period (Table 6.3, section 6.1.2). This may be the reason that the metal concentration in the bank sediment was higher than the metal concentration in bed sediment.

The <63µm sediment size fraction is the commonly used fraction for metal analysis in sediment not only due to its high metal sequestering ability, but also because it is the fraction commonly transported in rivers and ingested by benthic and aquatic organisms (Luoma and Rainbow, 2008). However, sediment monitoring using the <63µm particles will not only omit significant metal contribution from the 0.5-1mm and the 1-2mm particles of larger sizes but could potentially result in inadequate sample collection for laboratory analysis. A suitable alternative might be to carry out a pre-sampling program to study the physical characteristics of the river in terms of particle size, and determine the best method of sediment sampling.

There is a need to standardize the sediment particle size used for assessing sediment quality WFD. Several authors have used the <63µm fraction (Walling *et al*., 2003; Rodrigues and Formoso, 2006), some authors used the <2mm fraction (Gao *et al.,* 2010; Ruello *et al.*, 2011; Sutherland *et al.,* 2012), and others still used a combination of both fractions (Charlesworth and Lees, 1999b; Lin *et al.,* 2003). The data obtained from the Environment Agency of England and Wales on the Ravensbourne reported most of the metal concentration in sediment using the <2mm fraction and few results using the <63µm fraction (Environment Agency, 2010b). The British Geology Survey reported the background concentrations of metals in soil using the <2mm (Table 3.5, section 3.9). The <63µm fraction is often the focus of attention because it is most active fraction that is transported under the flow conditions of the majority of UK rivers (Owens *et al*., 2005; Guymer *et al*., 2010). Such a focus on the <63µm fraction, however, may actually result in significant sediment metals concentrations from large sediment fractions being ignored. Although the <63µm particle size is the fraction that is ingested by benthic organisms, sediment dwelling organisms are still exposed to contaminants on the other fractions (Luoma and Rainbow, 2008).

7.9.3 Heavy metal concentration in the different sediment compartments

Zinc, Pb and Cu were the dominant heavy metals retained in all sediment compartments, and high background concentrations of these metals in soil compared to Ni and Cd have been reported by the British Geological Survey (Table 3.6, section 3.9). These are also the most common heavy metals often reported in the urban environment (Pastorinho *et al.,* 2010; Martin, 2012). Lead is among the priority substances that environmental quality standard is required for by the WFD, and Cu and Zn are listed as specific pollutants (European Commission, 2006). The most common sources of Zn, Cu and Pb in the urban environment are from motor vehicles as a result of the wearing of brake lining and tyres, oil spills and emission from exhaust (Napier *et al*., 2008). These sources are likely to be the same for the Ravensbourne River. The Zn and Pb in the sediment could also arise from local soils, diffuse sources, atmospheric deposition and from run off from local road surfaces such as the major road in Catford, upstream of the sampling location (see section 3.3, Chapter 3)

The bank sediment contained higher concentration of metals in most of the sampling months compared to the bed and suspended sediment (Figure 7.4-7.6). This could be as a result of the smaller surface area of particles in the bank sediment compared to the bed and suspended sediment (see section 7.8.2 above). The concentration of metals in the bank sediment also had a stronger correlation with organic matter compared to the bed and suspended sediment (Table 7.7). Organic matter effectively sequesters heavy metals (Luoma and Rainbow, 2008) and could be a major reason for the high metal concentration in the bank sediment. The mineralogy of the bed, bank and suspended sediment also showed that the bank sediment had high concentration of clay minerals which are known to sequester heavy metals after the suspended sediment (Table 6.6, chapter 6). The bed sediment contained higher percentage of the non-reactive quartz mineral.

The results showed that concentration of heavy metals varied significantly for the bank sediment using the <63μm fractions (Table 7.2). This possibly implies that the <63μm bank sediment may have different sediment sources compared to the bed and suspended sediment. The results suggest not using the bank sediment for sediment monitoring since it may be unrepresentative of the sediments in the water course itself i.e. the bed and suspended sediment. It is likely to have different sediment sources compared to those sediment deposited by the river bank (Lee *et al*., 2003; Devesa-Rey *et al*., 2010; Zhao *et al*., 2010). Certainly, the bed and suspended sediment are the most widely used sediment compartments for sediment monitoring (Lee *et al.,* 2003; Ballantine *et al*., 2009). Clearly, the bed and suspended sediment are the sediment compartments that benthic and aquatic organisms are constantly exposed to, providing both habitat and food. Bank sediment is commonly sampled to determine the source of sediment and associated heavy metal contaminants that could enter the river as a result of bank erosion or transported to rivers during flood events. Arguably, the bank sediment could be excluded from any sampling regime since the key necessity is to determine exposure of aquatic organisms to contaminants through monitoring. It only becomes essential to determine the source of heavy metals and other pollutants when environmental quality standards are exceeded. In this case establishing the contribution of the bank sediments to pollutant concentrations by sampling the bank sediment becomes important as a prelude to designing remediation techniques and controlling pollutant

ingress. It may be useful when designing a sampling pattern for monitoring to sample both suspended and bed sediment initially, with the aim of first confirming similarities in metal concentration and ultimately reducing sampling to the bed or tube samplers only. Significant differences in metal concentrations between suspended and bed sediment would mean a continuation of sampling both compartments.

There was no significant difference ($p>0.05$) in the concentration of each heavy metal between the suspended tube samples in the section of the river sampled irrespective of where the tube samplers were placed. It appears that for a shallow river, and providing the sample area is in a straight stretch of river, the positioning of the integrated tube samplers makes little difference for monitoring. The most important factor is the concentration of suspended sediment in the river; low concentrations may not be unusual in urban rivers such as the Ravensbourne suggesting that multiple deployments of tube samplers may be necessary in order to obtain enough material for analysis. An alternative to this is the use of continuous pump centrifugation (see section 4.1.2.1, Chapter 4).

7.9.4 The impact of a flood event on metal concentration in bed, bank and suspended sediment

It is widely accepted that heavy metals from road surfaces are washed into a river from run-off during flooding events (Carton *et al.,* 2000). However, when the amount of rainfall is low, run off from urban surface is likely to permeate into surrounding soil or transport sediment to gully pots where it could be stored waiting for a big flood to re-suspend and flush it into the river. There were two storm events (Feb. 2011 and May 2012); however sediment samples could only be collected from bed, bank and suspended sediment during the May 2012 storm event due to high river level in the Feb. 2011 storm event. The bank sediment was the only sediment compartment sampled in the Feb. 2011 storm event.

There was no significant difference between the average monthly concentration of metals in the non-storm samples collected from January-December, 2011 (excluding the month of February 2011 storm event) and the concentration of metals in the storm samples (Table 7.3). A possible reason could be that sediment samples were

collected after the first flush samples. The first flush samples are the initial samples discharged by rainfall, usually after a long period of little or no rainfall (DEFRA and Environment Agency, 2005; Taylor and Owens, 2009). Higher concentrations of metals are often reported in sediment collected immediately after the start of runoff during storm events (Quek and Förster, 1993). The storm event (23.5mm of rainfall) occurred on the 28th April, 2012, however sediment and water samples were collected on the 5th May, 2012. The month of April 2012 had a total of 24 days of rainfall beginning on April 1st, and a maximum daily rainfall of 12.5mm was recorded four days before the storm event. There was no significant relationship between rainfall and heavy metal concentration in all the sediment compartments nor between discharge and metal concentration in all the sediment compartments (bed, bank and suspended sediment) except for Cd in the 63µm-2mm fraction of the bed sediment (Table 7.3 and 7.4). This implies that Cd was probably transported in the 63µm-2mm fraction, and that the Cd contribution would be missed if monitoring and sediment guidelines/standards were based solely on the <63µm fraction.

The most common sources of cadmium in the aquatic environment during the storm event include phosphate fertilizers, cigarette butts and street dust (Hutton, 1983; Muntau and Baudo, 1992; Baek and An, 2010). The use of Cd containing fertilizers on cultivated topsoils may also be a source of river contamination (Pan *et al*., 2010). The sampling site was next to a park area and it is not impossible that fertilizer use was a source of Cd in the river and bank. The increase in the concentration of metal in the suspended sediment during the May 2012 storm event may be as a result of contaminated sediment being carried in suspension rather than being deposited on river bed. The likely sources of heavy metal concentration in rivers with storm events are run off from road deposited sediment from materials detached from brake linings; tyres; and building/construction works (McKenzie *et al.*, 2009; Zafra *et al.,* 2011). The weak relationships between rainfall, discharge and metal concentration in sediment have also been reported by several authors (Leenaers, 1989; Walling *et al*., 2000).

7.9.5 Compliance of the Ravensbourne sediment metal concentrations with the draft UK sediment quality guidelines and sediment quality guidelines from other countries

The concentration of all the metals in the bed, bank and suspended sediment of the Ravensbourne River at the sampling location exceeded the draft UK threshold effect level (TEL) standard and the threshold effect standard for other countries such as The Netherlands, Belgium (Flanders), Australia and New Zealand, Canada and the United States (Florida), except for Cd in one of the four integrated suspended sediment sample (Table 7.9 and 7.10). In fact, the background concentrations of most of the heavy metals in the surrounding soil were also higher than the UK draft TEL and PEL sediment quality guidelines values. Clearly, the sediment in the River Ravensbourne at the sampling site does not comply with the UK draft sediment guidelines. The metal concentration in the river may have originated partly from diffuse pollution such as road run off, or from historical point source pollution located upstream of the sampling location such as cutlery manufacturing at Beckenham about 5.9km from sampling location (Table 3.1, section 3.4). Although, the Environment Agency reported a significant sewage pollution in Bromley (upstream of the sampling location) in June, 2010 (Table 3.3, section 3.8), this sewage pollution in the water column is likely to be diluted in the river as it travels away from source (Miller, 1996; Werkenthin *et al*., 2014), similarly some of the sewage materials will be deposited during transportation, especially in area where the river velocity is low (Walling *et al.,* 2000). The impact of the sewage pollution on the sampling location will be dependent on other factors such as the quantity and the duration of the sewage pollution, and possibly on weather condition such as rainfall which can increase the level of dilution (Coulthard and Macklin, 2003; Palmer *et al.,* 2011). Another possible source of metal pollution upstream is the electroplating company in Lower Sydenham which was prosecuted in 2007 for releasing heavy metals (possible, Cu, Ni and Zn) into the Ravensbourne.

The concentration of Cu, Ni, Pb, Cd and Zn in all sediment compartments reflect a combination of the natural geochemical background, anthropogenic impacts (see above) and possibly mixing effects of contaminant sources within the Ravensbourne catchment (Luoma and Rainbow, 2008; Stockdale *et al.,* 2010). Inevitably metals in the overlying water could be one source of metal pollutants for the river sediments

because the river pH varies between the neutral and alkaline range (Table 5.1, section 5.1), which implies that most metals in the water column are likely to be adsorbed onto the sediment surface (Atkinson *et al*., 2007). If it is accepted that the Ravensbourne is fairly representative of small urban rivers with significant metal inputs from anthropogenic diffuse as well as point source pollution, it seems relatively likely that the quality guidelines will be breached by most rivers of this type in the UK. In addition, metal pollutants are long-lived in the environment and any historical contaminant concentrations are likely to persist in the aquatic environment, making metal sediment quality a chronic and persistent problem. One issue that may be relevant in setting metal sediment quality standards is consideration of the bioavailability of the metals rather than simply setting sediment standards or guidelines based on the total concentrations.

7.9.6 The relationship between the concentrations of heavy metal in sediment compartments to that in the overlying water column

The results show that there were no consistencies in the relationship between the concentration of metals in the bed and bank sediment with those in the water column (Table 7.11). This is likely to be as a result of the neutral to alkaline pH for the water column, suggesting most metal contaminants will be bound to sediment. This however does not imply that the Ravensbourne sediment are not contributing to the poor water quality, pollutants from sediment are released back into the water column during changes in the river characteristics such as low (acidic) pH (Atkinson *et al*., 2007), which did not occur during the sampling period. One of the major causes of river acidification is acid rain, however, the reduction in the emission of sulphur have helped in the reduction of acid rain in both the UK and other European rivers (Wright *et al*., 2005). Other climatic factors that are likely to increase acidification of rivers are higher temperature, wetter winters and increase in summer drought (Evans *et al.,* 2008; Whitehead *et al*., 2009). There was no relationship in this study between metal concentration in the water column and pH i.e. metal concentration did not decrease with increasing pH (Table 5.1, section 5.1). Since most natural rivers have a pH between neutral and slightly alkaline, most metals are likely to be bound to sediment, irrespective of the river size or depth unless spillage of acidic compounds changes local environmental conditions. The heavy metals likely to be released from

sediment into the overlying water are the fractions retained in the mobile and mobilsable phase (exchangeable, carbonate, iron/manganese phase and the organic) (see Chapter 8).

7.9.7 Variations total metal extraction techniques

One of the major differences between total extraction experiments is whether or not they use hydrofluoric acid (Hseu *et al.,* 2002). Hydrofluoric acid (HF) is often used for the complete dissolution of silicate minerals in sediment. However, many studies on total metal concentration in sediment are beginning to focus on the use of a combination of less toxic and easier to use acids such as aqua regia ($1HNO_3$:3HCl) (Environment Agency, 2006; Sakan *et al.,* 2011). The results for total metal extraction using the aqua regia ($1HNO_3$:3HCl) and $HF/HClO_4/HNO_3$ in this study indicated that there were no significant difference between the two extracting solutions (Table 7.12). A similar result was reported by Ščančar, *et al*. (2000) for Pb, Cu and Zn comparing a mixture of $HF/HNO_3/HClO_4$ and aqua regia extraction of metals from sediment. Hseu *et al*. (2002) also reported no significant difference in the total concentration of Cu, Ni and Zn comparing the aqua regia method with $HF\text{-}HNO_3\text{-}HClO_4\text{-}H_2SO_4$ total extraction method. However, the concentration of Cd and Pb were significantly different comparing both extraction methods, the total concentration of Cd was higher with the $HF\text{-}HNO_3\text{-}HClO_4\text{-}H_2SO_4$ while the total concentration of Pb was higher using aqua regia. The low concentration of Pb extracted by $HF\text{-}HNO_3\text{-}HClO_4\text{-}H_2SO_4$ was attributed to the precipitation of Pb and the interference of $PbSO_4$ (Hseu *et al.,* 2002). There was no such effect found in this study.

In general, the total metal concentrations in sediment do not vary with extracting solution for the Ravensbourne sediment. The use of strong concentrated acid mixtures with or without hydrofluoric (HF) acid depends on the aims of the survey but is probably not necessary for metal monitoring for toxicity to aquatic organisms as most of the metals retained in silicates are hardly mobile. Although hydrofluoric acid is commonly used to dissolve silicates minerals, aqua regia has gained wider acceptance in recent years due to an increased awareness of the need to monitor the bioavailable fractions rather than the immobile fraction that is retained in silicate

minerals. In not releasing metals from silicate minerals, aqua regia may provide a better gauge of metal bioavailability than using HF, as well as having the advantage of faster, easier and safer use required for monitoring programmes. Aqua regia is also commonly used by regulatory bodies such as the Environment Agency and the International organization for Standardization (ISO 11466.3) (Environment Agency, 2006; Peña-Icart *et al*., 2011). It may be a pragmatic approach to adopt the aqua regia method for regular monitoring of sediment environmental quality standards as the Environment Agency currently has.

7.10 Summary

The concentrations of metals vary with sediment sizes. Higher concentrations of heavy metals were associated with the <63µm fraction, and the bank sediment contained higher concentrations of most of the metals compared to the bed and suspended sediment. Organic matter seem to play a significant role in the concentration of metals in the bank sediment as there was a significant relation between organic matter and metal concentration only in the bank sediment. Zinc had the highest concentration of all the metals and Cd had the least concentration. Overall, there was no significant difference between the metal concentration in the bed and suspended sediment using the <63µm fraction of the bed sediment. The concentration of metals in sediment exceeded the UK draft sediment quality guidelines, and there were no significant difference between total metal extraction using the HF/$HClO_3$ /HNO_3 and aqua regia extracting solution.

Chapter 8

Fractionation of heavy metals in sediment

8.0 Introduction

The need to consider the bioavailable concentration of heavy metals for developing sediment quality guidelines in place of the traditionally used total metal concentration is gaining recognition (McCauley *et al.,* 2000; Crane, 2003). The environmental effect of heavy metals is linked to their mobility and bioavailability rather than the total metal concentration (Passos *et al.,* 2010). Assessing the bioavailable concentration of heavy metals in sediments requires the use of sequential extraction procedures. However, these are operationally defined (i.e. depend on the method and reagent used) and different results have often been reported with different sequential extraction techniques (Sutherland and Tack, 2003). The Tessier *et al*. (1979) method, which is the most widely used and generally accepted method for examining metal speciation in sediment, and the Maiz *et al.* (1997), a short modified sequential extraction method, was used to study differences in metal speciation between the bed, bank and suspended sediment. The possibly implication for sediment monitoring is examined in this chapter.

8.1 Maiz *et al.* (1997) sequential extraction: The chemical phase distribution using the Maiz *et al*. (1997) method shows speciation for three phases, the exchangeable, mobilisable and residual phases. The exchangeable and mobilisable phases are considered to be bioavailable. The results for the sequential extraction using the Maiz *et al.* (1997) indicated that most of the heavy metals were retained in the residual phase of each sediment compartment and size fraction, so not, therefore, readily bioavailable (Figure 8.1 - 8.5). About 80% of all the heavy metals were retained in the residual fraction of the bed and bank sediment compartments for the majority of the sampling period, including the May 2012 storm sample. The sole exception were the results for November in the <63µm bed sediment when between 50 and 70% of Cd, Ni and Zn were retained in the bioavailable fraction (exchangeable and mobilsable fraction), and for Cd in the bank sediment where up to 40% are bioavailable (Figure 8.3 and 8.4). Likewise, the concentration of Ni for the May 2012 storm sample showed that between 67-90% of the Ni was bioavailable in

the bed sediment (Figure 8.1 and 8.2). About 99% of Pb retained in the <63μm bank sediment was not bioavailable (Figure 8.3).

The percentage of the bioavailable fraction varied slightly with metals in the different sediment fractions (<63μm and the 63μm-2mm). The percentage of the bioavailable fraction was higher in the <63μm bed sediment fraction for Cd, Ni and Zn, Cu did not show much variation while Pb was more bioavailable in the 63μm-2mm bed sediment fraction (Figure 8.1 and 8.2). However, the bank sediment showed that the percentage of the bioavailable fractions was higher in the 63μm-2mm sediment fraction compared to the <63μm sediment fraction (Figure 8.3 and 8.4).

The Maiz *et al*. (1997) sequential extraction was carried out for only 13 available suspended sediment samples (for the months of January, April and July samples) due to insufficient sediment mass in the remaining samples. The results indicated that between 25-75% of Zn retained in the suspended sediment in the month of April was bioavailable (Figure 8.5). The rest of the sediment samples analysed for the remaining metals only contained between 0 - 22% in the bioavailable fraction.

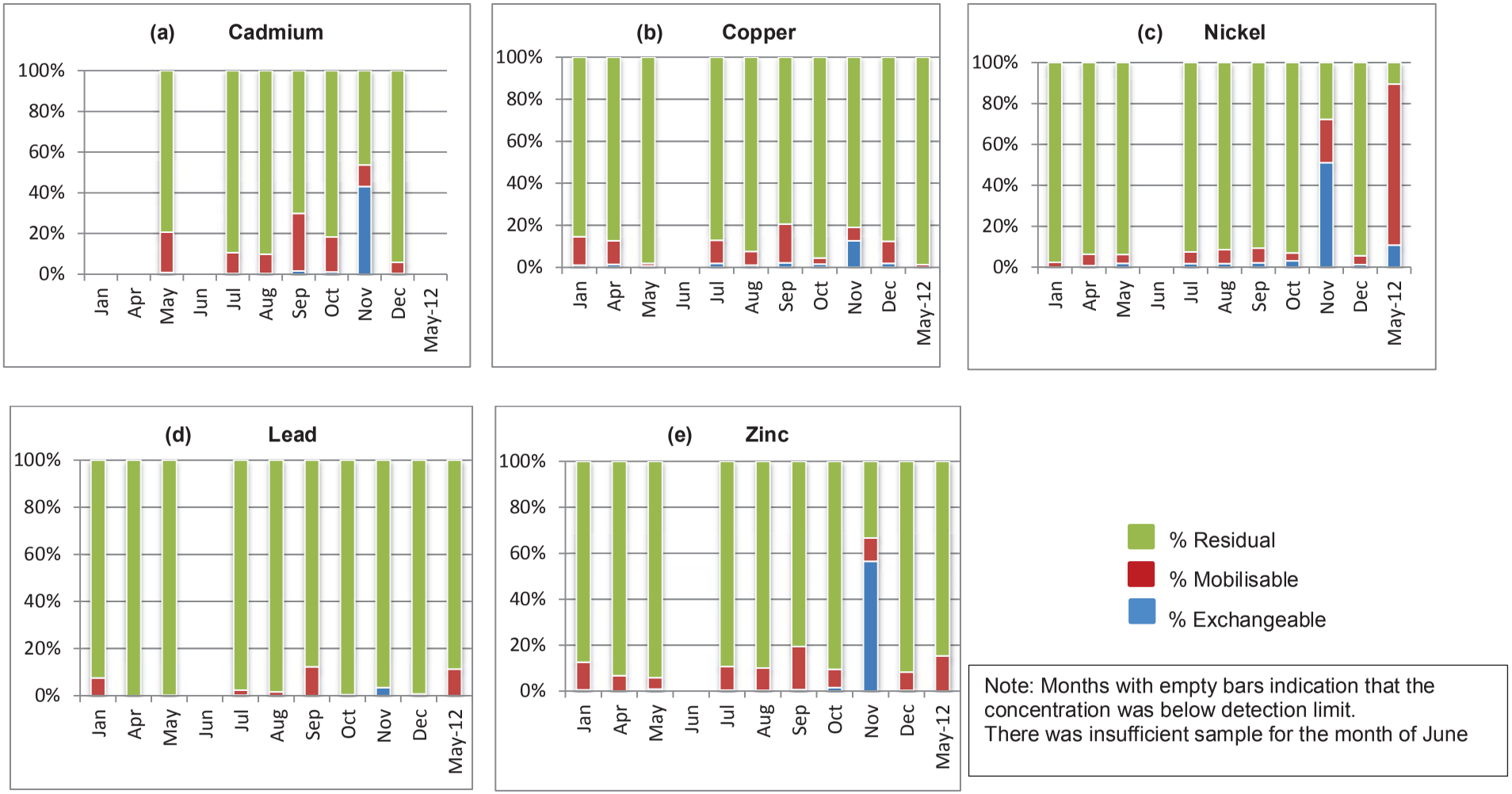


Figure 8.1The mean percentage exchangeable, mobilisable and residual phase by Maiz *et al.* (1997) (a) Cd (b) Cu (c) Ni (d) Pb (e) Zn in <63µm bed sediment at different sampling times (n=3 replicate extraction)

Figure 8.2 The mean percentage exchangeable, mobilisable and residual phase by Maiz *et al.* (1997) (a) Cd (b) Cu (c) Ni (d) Pb (e) Zn in 63µm-2mm bed sediment at different sampling times (n=3 replicate extraction)

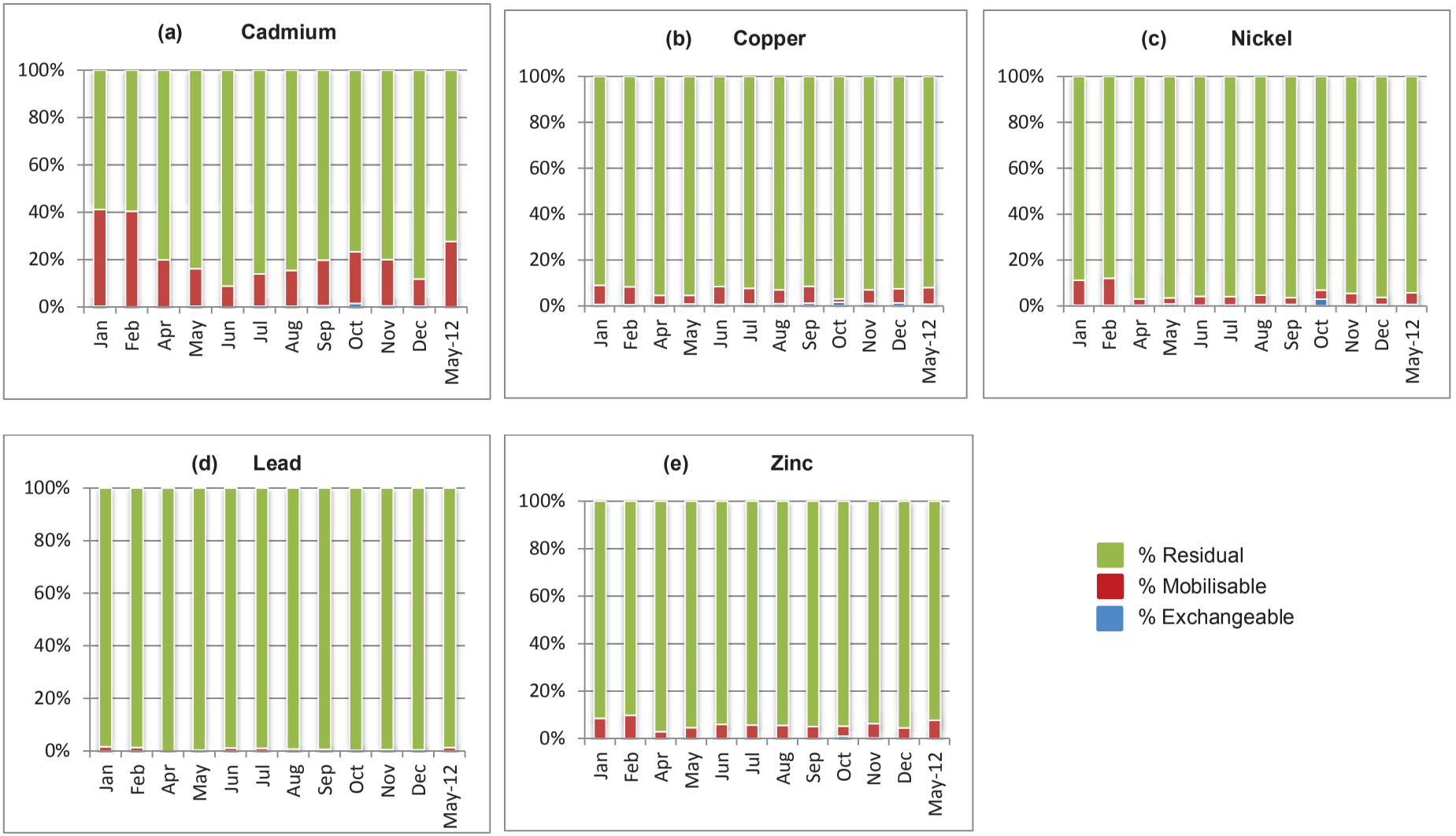


Figure 8.3 The mean percentage exchangeable, mobilisable and residual phase by Maiz *et al*. (1997) (a) Cd (b) Cu (c) Ni (d) Pb (e) Zn in <63µm bank sediment at different sampling times (n=3 replicate extraction)

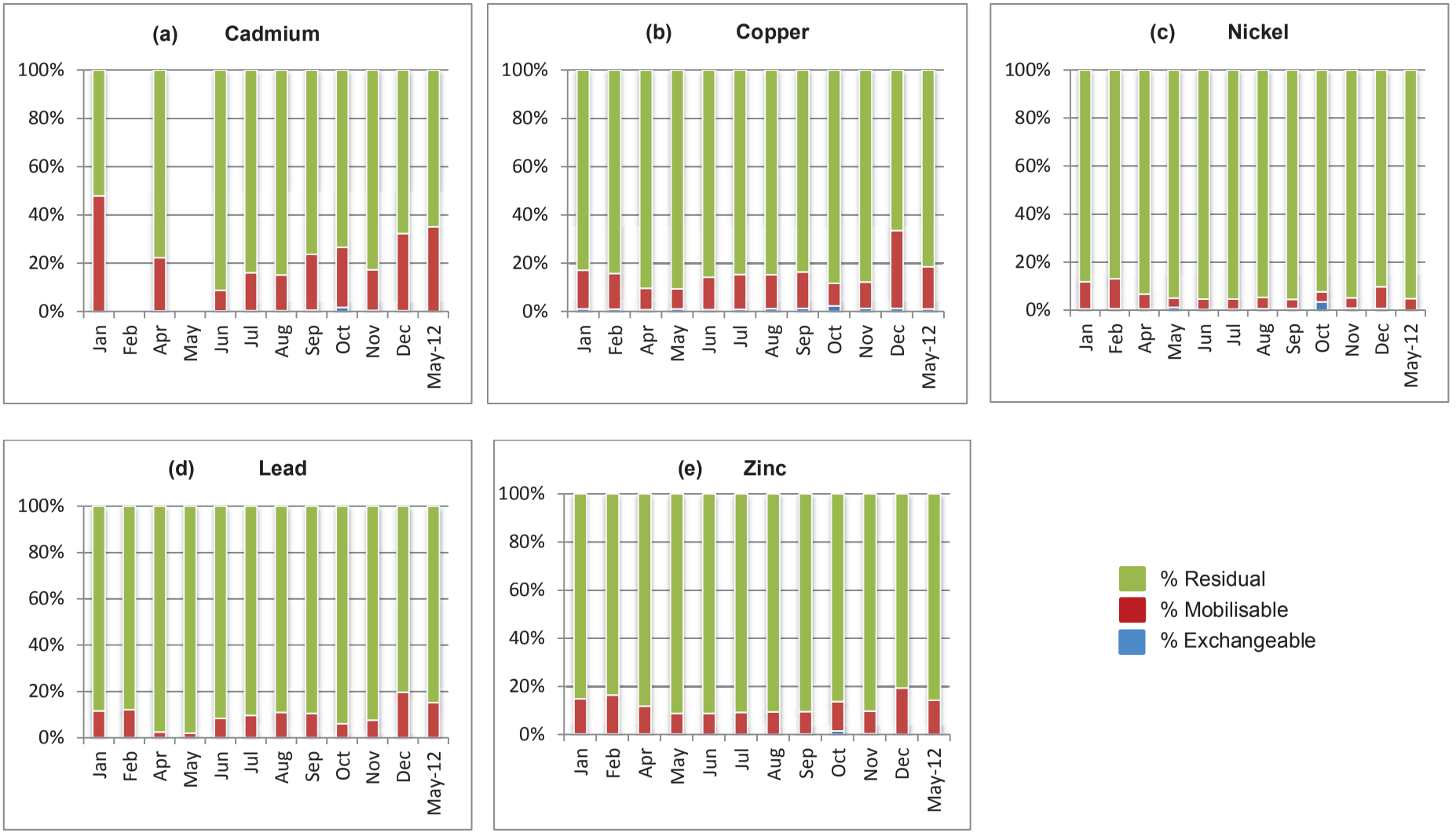


Figure 8.4 The mean percentage exchangeable, mobilisable and residual phase by Maiz *et al.* (1997) (a) Cd (b) Cu (c) Ni (d) Pb (e) Zn in 63µm-2mm bank sediment at different sampling times (n=3 replicate extraction)

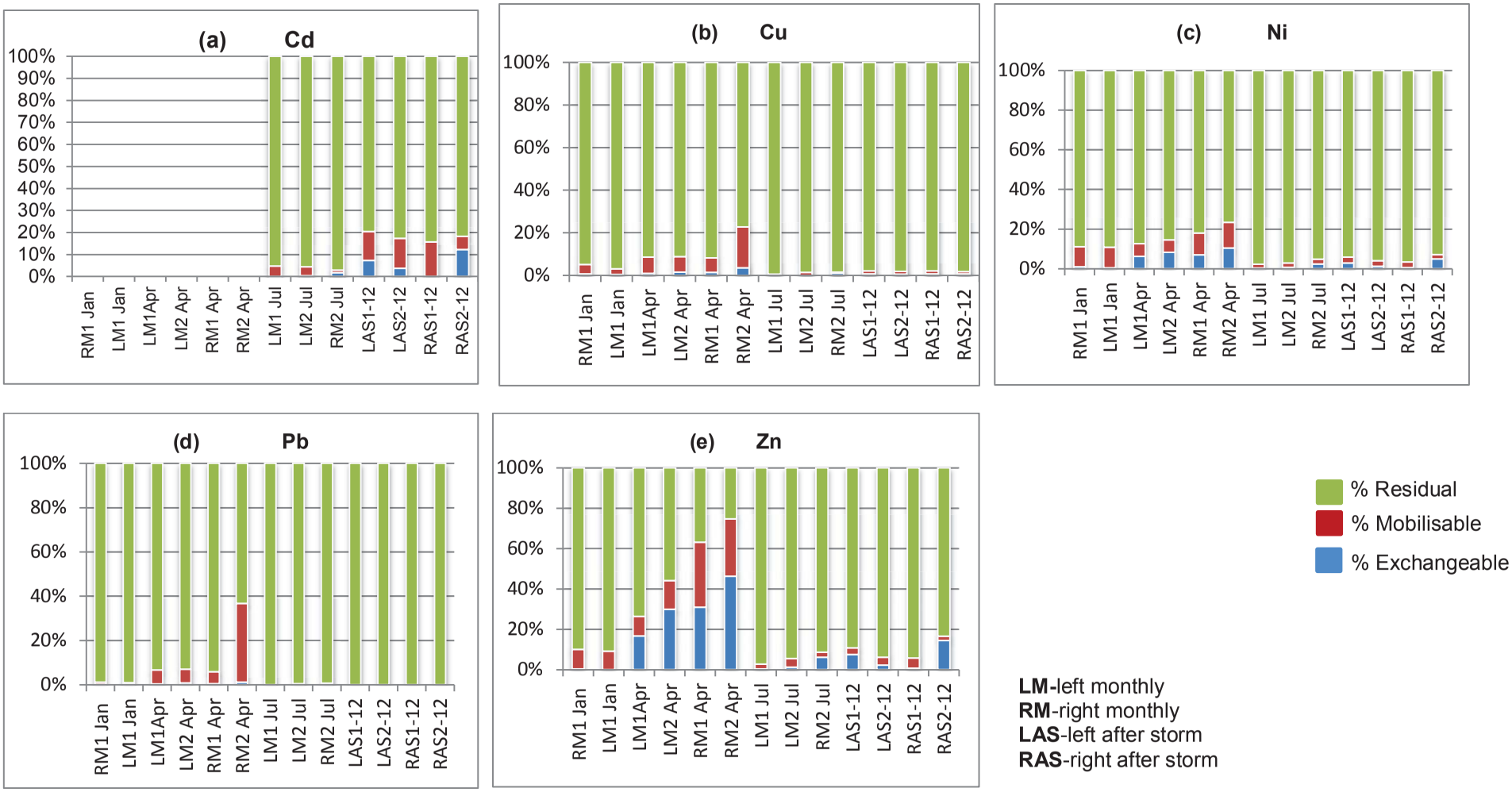


Figure 8.5 The mean percentage exchangeable, mobilisable and residual phase by Maiz *et al.* (1997) (a) Cd (b) Cu (c) Ni (d) Pb (e) Zn on selected suspended sediment at different sampling period (n=3 replicate extraction)

8.2 Tessier *et al*. (1979) sequential extraction

The Tessier *et al*. (1979) sequential extraction was only carried out on selected sediment samples (July 2011 sediment and the May 2012 storm sediment sample). The Tessier *et al.* (1979) method fractionates metals into the exchangeable, carbonate, Fe/Mn, organic and residual phases. The Tessier *et al.* (1979) method indicated that at about 15% (for Cd) to 90% (for Zinc) of the metals are bioavailable (exchangeable, carbonate, Fe/Mn and organic phase). Copper was predominantly associated with the organic phase while other metals were mainly associated with the Fe/Mn and residual phases. The chemical association of heavy metals in each phase showed slight variations with metal and sediment compartment (Figure 8.6). Zinc was the most mobile of all the heavy metals with only approximately 20% of the total zinc retained in the residual fraction (Figure 8.6).

The bioavailable concentration of the heavy metals using the Tessier *et al*. (1979) method follows the order Zn>Cu>Pb>Ni>Cd for all the sediment compartments.

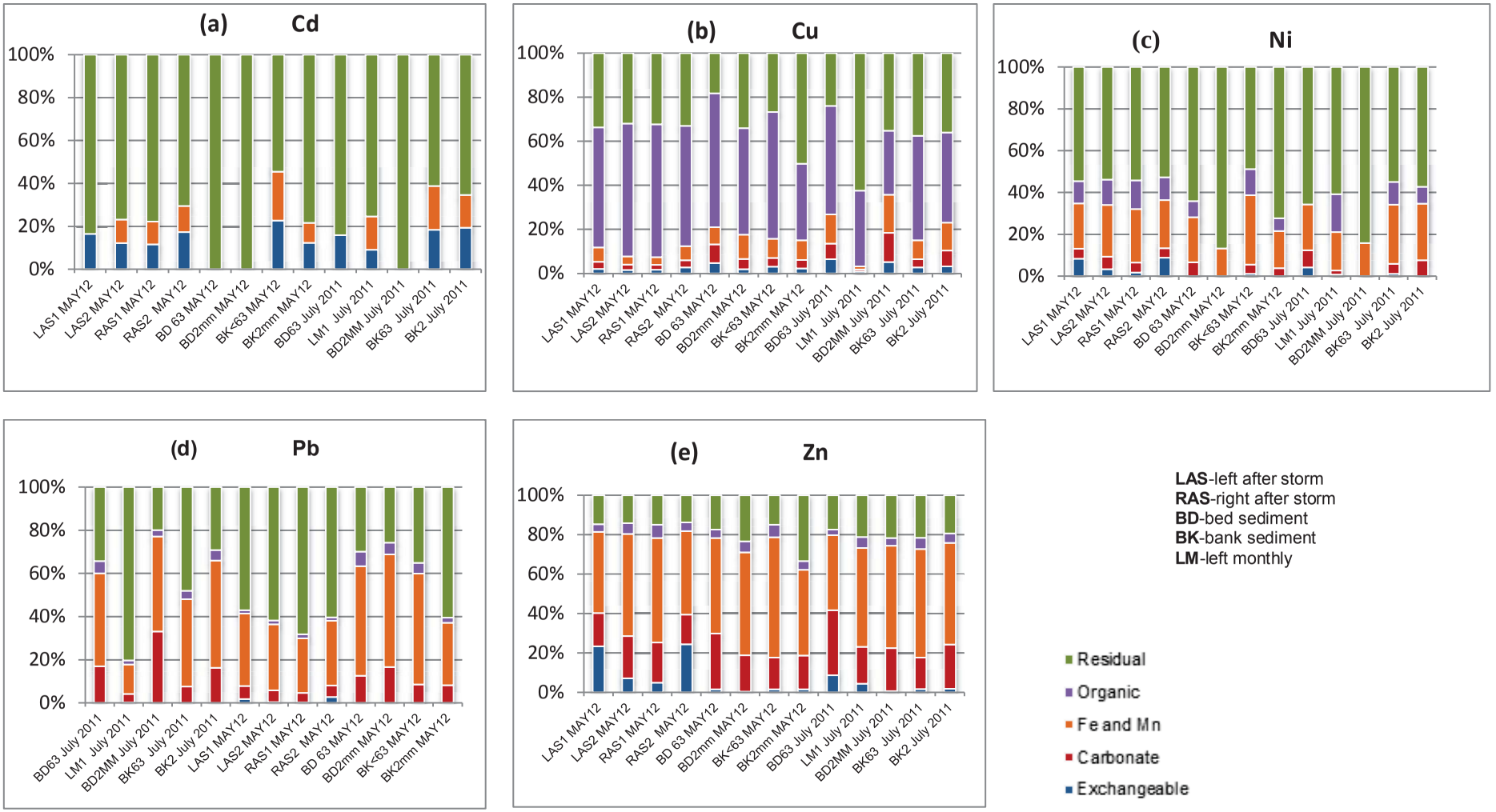


Figure 8.6 The mean percentage of the exchangeable, carbonate, Fe/Mn, organic and residual phase by Tessier *et al.* (1979) (a) Cd (b) Cu (c) Ni (d) Pb (e) Zn in storm (May 2012) and non- storm (July 2012) samples (n=3)

8.3 Variations in results between sequential extraction techniques (Tessier *et al.,* 1979 and Maiz *et al.,* 1997) and comparison with sediment EQS

A comparison of the Maiz *et al.* (1997) and Tessier *et al*. (1979) method using the bed, bank and suspended sediment storm sample (May 2012) and non-storm sample (July 2011) are presented for the sum of the total mobile metal phases in sediment (Table 8.1 - 8.5). The Tessier *et al.* (1979) method separates metals into more phases than the Maiz *et. al.* method. The results from the Tessier *et. al.* method indicated that most of the metals were mobile (Figure 8.6), while the Maiz *et.al.* (1997) method suggested that most of the metals were immobile (that is associated with the residual fraction) (Figure 8.1-8.5). Over 80% of majority of the metals were retained in the residual phase in the Maiz *et al.* (1997) method compared to the Tessier *et al*. (1979) method where the percentage of metals retained in the residual fraction varied from 15% (for Zn) to 100% for Cd (Figure 8.6).

The sum of the mobile fractions of the Maiz *et al.* (1997) method (exchangeable and mobilisable) always had lower concentrations of metals than the Tessier *et al.* (1979) mobile phases (exchangeable, carbonate, Fe/Mn, and organic phase) for all the metals except for cadmium in the storm samples (Table 8.1-8.5). Unlike other metals, the Maiz *et al*. (1997) method extracted higher concentration of Cd in the storm samples compared to the Tessier *et al*. (1979) method (Table 8.1).

The differences between extracting solutions using the Maiz *et al.* (1997) methods (mobile + mobilisable) and the Tessier *et al*. (1979) methods (exchangeable + carbonate + Fe/Mn +organics) was significantly difference ($p<0.0001$) for the concentration of each heavy metals retained in the mobilisable phases of all sediment (including the different sediment sizes and compartments) using the Mann Whitney non-parametric test except Cd (Table 8.6).

Table 8.1 The total bioavailable concentration of the Tessier *et al.* (1979) methods (exchangeable, carbonate, Fe/Mn and organic) and the Maiz *et al.* (1997) methods (exchangeable and mobilisable) for Cd

	Maiz *et al.(*1997), mgkg^{-1}	Tessier *et al.* (1979), mgkg^{-1}
<63µm bed July 11	0.28	0.80
LM1 July 2011	0.21	2.30
63µm-2mm bed July 11	<	<
<63µm bank July 11	0.72	3.38
63µm-2mm bank July 11	0.39	1.20
LAS1 May 12	3.11	0.93
LAS2 May 12	3.47	1.52
RAS1 May 12	3.27	1.48
RAS2 May12	3.51	1.89
<63µm bed May 12	2.11	<
63µm-2mm bed May 12	0.44	<
<63µm bank May 12	9.35	2.86
63µm-2mm bank May 12	4.84	1.19

< indicates below the detection limit

LM-left monthly**, LAS-** left after storm**, RAS- r**ight after storm

Draft UK-Threshold effect level (TEL) for Cd = 0.596mgkg^{-1}

Draft UK-Predicted effect level (PEL) for Cd = 3.53mgkg^{-1}

Table 8.2 The total bioavailable concentration of the Tessier *et al.* (1979) methods (exchangeable, carbonate, Fe/Mn and organic) with the Maiz *et al.* (1997) methods (exchangeable and mobilisable) for Cu

Cu	Maiz *et al.(*1997), mgkg^{-1}	Tessier *et al.* (1979), mgkg^{-1}
<63µm bed July 11	29.18	158.74
LM1 July 2011	1.41	127.72
63µm-2mm bed July 11	3.33	17.95
<63µm bank July 11	11.79	110.69
63µm-2mm bank July 11	9.57	44.07
LAS1 May 12	4.52	163.12
LAS2 May 12	5.38	195.79
RAS1 May 12	5.99	185.02
RAS2 May12	4.7	159.92
<63µm bed May 12	23.23	129.12
63µm-2mm bed May 12	2.73	18.81
<63µm bank May 12	13.96	111.22
63µm-2mm bank May 12	11.75	51.70

< indicates below the detection limit

LM-left monthly**, LAS-** left after storm**, RAS- r**ight after storm

Draft UK-Threshold effect level (TEL) for Cu =36.7mgkg^{-1}

Draft UK-Predicted effect level (PEL) for Cu = 197.0mgkg^{-1}

Table 8.3 The total bioavailable concentrations of the Tessier *et al.* (1979) method (exchangeable, carbonate, Fe/Mn and organic) and the Maiz *et al.* (1997) methods (exchangeable and mobilisable) for Ni

Ni	Maiz *et al.*(1997), mgkg^{-1}	Tessier *et al.* (1979), mgkg^{-1}
<63µm bed July 11	2.51	11.18
LM1 July 2011	0.95	21.49
63µm-2mm bed July 11	0.19	1.77
<63µm bank July 11	1.53	23.38
63µm-2mm bank July 11	0.83	9.49
LAS1 May 12	2.01	18.46
LAS2 May 12	1.78	20.81
RAS1 May 12	1.46	20.14
RAS2 May12	2.91	19.25
<63µm bed May 12	1.01	9.41
63µm-2mm bed May 12	<	1.69
<63µm bank May 12	1.78	20.02
63µm-2mm bank May 12	0.83	8.80

< indicates below the detection limit

LM-left monthly**, LAS-** left after storm**, RAS- r**ight after storm

Draft UK-Threshold effect level (TEL) for Ni = 18.0 mgkg^{-1}

Draft UK-Predicted effect level (PEL) for Ni = 35.9 mgkg^{-1}

Table 8.4 The total bioavailable concentrations of the Tessier *et al.* (1979) method (exchangeable, carbonate, Fe/Mn and organic) and the Maiz *et al.* (1997) methods (exchangeable and mobilisable) for Pb

Pb	Maiz *et al.*(1997), mgkg^{-1}	Tessier *et al.* (1979), mgkg^{-1}
<63µm bed July 11	5.59	221.09
LM1 July 2011	0.24	94.24
63µm-2mm bed July 11	13.17	63.15
<63µm bank July 11	6.73	404.31
63µm-2mm bank July 11	28.03	228.07
LAS1 May 12	<	134.13
LAS2 May 12	<	147.08
RAS1 May 12	<	113.03
RAS2 May12	<	125.93
<63µm bed May 12	22.41	155.12
63µm-2mm bed May 12	21.55	93.89
<63µm bank May 12	2.73	339.93
63µm-2mm bank May 12	30.47	204.69

< indicates below the detection limit

LM-left monthly**, LAS-** left after storm**, RAS- r**ight after storm

Draft UK-Threshold effect level (TEL) for Pb = 35.0 mgkg^{-1}

Draft UK-Predicted effect level (PEL) for Pb = 91.3 mgkg^{-1}

Table 8.5 The total bioavailable concentrations of the Tessier *et al.* (1979) method (exchangeable, carbonate, Fe/Mn and organic) and the Maiz *et al.* (1997) methods (exchangeable and mobilisable) for Zn

Zn	Maiz *et al.(*1997), mgkg^{-1}	Tessier *et al.* (1979), mgkg^{-1}
<63µm bed July 11	47.39	441.04
LM1 July 2011	23.82	757.33
63µm-2mm bed July 11	8.73	90.17
<63µm bank July 11	37.66	567.26
63µm-2mm bank July 11	28.04	242.02
LAS1 May 12	67.11	612.51
LAS2 May 12	53.56	764.00
RAS1 May 12	48.12	731.14
RAS2 May12	122.86	672.22
<63µm bed May 12	49.72	276.11
63µm-2mm bed May 12	11.39	109.09
<63µm bank May 12	52.33	539.25
63µm-2mm bank May 12	28.49	246.21

< means less than detection limit

LM-left monthly**, LAS-** left after storm**, RAS- r**ight after storm

Draft UK-Threshold effect level (TEL) for Zn =123.0 mgkg^{-1},

Draft UK-Predicted effect level (PEL) for Zn= 315.0 mgkg^{-1}

Table 8.6 Spearman correlation and Mann Whitney comparison of the bioavailable heavy metals between the Maiz *et al.* (1997) and Tessier *et al*. (1979) sequential extraction methods

Heavy metals	Mann Whitney test (n=13)
Cd	P=0.37
Cu	P<0.0001
Ni	P<0.0001
Pb	P<0.0001
Zn	P<0.0001

A comparison of the sum of the bioavailable fractions of the Maiz *et al*. (1997) and the Tessier *et al*. (1979) with the draft UK sediment quality guidelines in order to check compliance if sediment standards were based on the bioavailable fraction was made. The bioavailable concentrations extracted using the Maiz *et al*. (1997) method were predominantly below the threshold and probable effect concentrations for all the metals except for the concentration of Cd in the storm samples. The bioavailable fraction of the metals extracted using the Tessier *et al.* (1997) method

were consistently above the threshold effect level but below the probable effect level for Cd, Cu and Ni (Table 8.1- 8.3). Finally, the bioavailable concentrations of Zn and Pb were higher than the draft UK TEL and PEL values in most of the sediment samples using the Tessier *et al*. (1979) extraction method (Table 8.4 and 8.5)

8.4 Discussion

The main challenge of sequential extraction experiments is that they are operationally defined. This is clearly reflected in the results of this study where different bioavailable concentrations have been obtained from using the Maiz *et al.* (1997) and the Tessier *et al*. (1979) sequential extraction methods.

Sequential extraction using the Maiz *et al*. (1997) sequential extraction indicated that most of the metals were not bioavailable (retained in the residual fraction). Similar results were obtained for soil samples collected from highly polluted area (mining activity, smelting factory and highway area) of Spain where about 80% of most of the metals were retained in the residual fractions except for Cd where between 40-70% were retained in the residual fraction (Maiz *et al*., 1997). Sequential extraction using the Tessier *et al*. (1979) method indicated a similar phase apportionment of metal in the bed, bank and suspended sediment in both the storm and the non-storm samples. Cadmium and Ni were mainly associated with silicate minerals (residual fraction); Cu was mostly associated with organic phase and Pb was mostly associated with the Fe/Mn and the residual phase. Similar results have been published by several authors on the association of metals with a particular phase. The result for Cu being associated mainly with the organic phase is consistent with the findings of several authors (Li *et al.,* 2007; Pertsemli, and Voutsa, 2007; Vicente-Martorell *et al.,* 2009). This is usually attributed to the ease at which Cu forms complexes with organic compounds due to the high stability constant of organic copper compounds (Pertsemli, and Voutsa, 2007; Vicente-Martorell *et al.,* 2009). Zn was predominantly associated with the Fe/Mn and carbonates phases, and was the most enriched metal in the sediment. Similar results of metal association have been published by other authors (Alagarsamy, 2009; Saulais *et al.,* 2011). A study reported by Charlesworth *et al*. (2003) on heavy

metal concentration in deposited street dust of a large urban catchment, showed the highest percentage of Cd to be associated with the exchangeable fraction López-Sánchez *et al*. (1996) reported Cd as the most bioavailable metal with up to 30% of total concentration in the exchangeable fraction. The study on the Ravensbourne suggested that Cd was primarily associated with the residual fraction. This difference may simply be a reflection of the importance of the mineralogy and reactivity of the sediment and road dust.

It was difficult to carry out direct comparison of the Maiz *et al*. (1997) and the Tessier *et al.* (1979) due to the different extraction phases involved in both sequential extraction method, and different extracting solutions and concentrations used to extract each phase. The sum of the bioavailable fractions obtained using the Maiz *et al*. (1997) and the Tessier *et al.* (1979) varied significantly. These differences in the concentration of bioavailable heavy metals using the different sequential extraction methods are mainly due, of course, to the use of different reagents, different agitation temperatures and times, and different reaction times (Hlavay *et al.,* 2004; Bacon and Davidson, 2008). Different reagents might be effective in extracting certain metals compared to other metals, for example, the reagents ($CdCl_2$ + DTPA) used in this research appears to have extracted more Cd in the total bioavailable phase of the Maiz *et al.* (1997) method compared to the reagents ($MgCl_2$+ NaOAc+ (NH_20H-HCl+HOAc) + (HNO_3 + H_2O_2)) used to extract the total bioavailable phase (exchangeable, carbonate, Fe/Mn and organic phase) of the Tessier *et al*. (1979) method particularly for most of the storm samples (Table 8.1 - 8.5). The variations in sediment characteristics such as organic matter content and contaminant mixtures (other inorganic and organic contaminants) might favour some extractants over others (Luoma and Rainbow, 2008).

The use of the bioavailable fraction rather than the total metal concentration in setting environmental quality standards for heavy metals has been widely suggested (Tack and Verloo, 1995; Rodrigues and Formoso, 2006; Prica *et al*., 2010). Some of the major weaknesses with sediment quality guidelines are that they do not predict how much of the contaminants are bioavailable (Simpson *et al.,* 2011). The bioavailable fraction is usually in the dissolved form (solution), however metal could also be bioavailable when contaminated sediment are ingested by

benthic organisms. Dietary sources have been identified as a significant route in which aquatic organisms are exposed to heavy metals (USEPA, 2007). A comparison of the sum of the bioavailable fractions for the Tessier *et al*. (1979) method (exchangeable, carbonate, Fe/Mn and organic) and the Maiz *et al.,* 1997 method (exchangeable and mobilisable) using the Mann-Whitney test indicated a significant difference between the two methods of sequential extraction for all the heavy metals except for Cd (Table 9.7). It would be expected that these bioavailable fractions should be broadly comparable, but this is not the case. This presents a challenge if sediment quality standards are to be based on the bioavailable fractions as the Ravensbourne sediment will comply with the draft UK sediment quality standards using Maiz *et al.* (1997) but fails to comply using the Tessier *et al.* (1979).

There is a need for standardization of techniques to analyse metal concentration in sediment and a need to develop analytical techniques that will give an accurate measurement of the bioavailable metal concentration. It may be the case that field and laboratory studies of the ecotoxicological impact of sediment associated metal on sediment dwelling organisms should be examined on the basis of their correlations with the measures of bioavailability given by various sequential extraction techniques. This might help establish the best method to measure bioavailability of metals for use as an indicator of risk and in the establishment of appropriate sediment quality standards based on bioavailability. The Environment Agency does not consider metal bioavailability in current sediment metal monitoring. Sediments are only analysed for total metal concentration using aqua regia with sediment quality standards being assessed using the total metal concentration (Environment Agency, 2006).

If EQSs are to be based on bioavailable fraction of metals then using the Maiz *et al.* (1997) sequential extraction method may potentially provide insufficient protection for the environment. This method appears to provide a substantial bias towards recording metals as associated with the residual phase i.e. non-bioavailable. The main challenge is likely to be identifying the sequential extraction method that is right for a particular sediment sample. The Tessier *et al.* (1979) remains the most widely used method for sequential extraction and provides more detailed information about metal speciation phases in sediment, and many sequential

extractions methods are a modified from the Tessier *et al.* (1979) method. Although time consuming, the Tessier *et al.* (1979) method probably offers the most appropriate method to use in determining bioavailability of metals but unfortunately because of the complexity of the method it is not realistic to use as a standard analytical procedure for regular monitoring.

Chapter 9
Phosphorus

9.0 Introduction

Phosphorus is a highly reactive non-metallic element in the nitrogen group that is capable of reacting with metals to form insoluble complexes effectively immobilising the metals (Cao *et al.,* 2003). The most common ways phosphorus (P) is released into the aquatic environment are from the treated waste water, run-off from farmland (Smil, 2000) or flowerbeds in the Ladywell Park for the case of the Ravensbourne River. The concentration of phosphorus in sediment was investigated to assess if there was any relationship between the concentration of selected heavy metals and the concentration of P, and if phosphorus plays any role in reacting with metal to form insoluble complexes.

9.1 Total concentration of phosphorus in sediment

The total concentration of phosphorus was an order of magnitude higher (over 3 times) than the concentration of the selected heavy metals (mg/kg) in the non-storm and storm event sediment samples (Table 9.1 and Table 9.2). The concentration of P varied for each month and for the different compartments. Higher concentrations of P were found in the suspended sediment compared to the bed and bank sediment; the 63μm-2mm fraction of the bed sediment had the lowest concentration of the phosphorus (Table 9.1). In general for most of the sampling period, the total concentration of P in the different sediment compartments followed the order: suspended>bank>bed.

The concentration of P in the different sediment compartments was significantly different ($p<0.001$) using the Kruskal-Wallis test. The concentration of P in the bank sediment varied slightly over the sampling months compared to the concentration in the bed and suspended sediment. There was a decrease in the concentration of P in the storm sample and in the bed and bank sediment compared to the non-storm sample (Table 9.2), and the concentration of P was higher in the suspended sediment during the flood event.

Table 9.1 The total concentration (±SD) of phosphorus and heavy metals in selected sediment samples (Oct.-Dec. 2011) (n=3)

	Sample	P, mg/kg	Cd, mg/kg	Cu, mg/kg	Ni, mg/kg	Pb, mg/kg	Zn, mg/kg
October, 2011	Left monthly 1	3159.1±0.0	0.9±0.0	109.7-±0.0	47.5±0.0	141.0±0.0	289.7±0.0
	Left monthly 2	1490.3±0.0	0.4±0.0	55.7±0.0	26.7±0.0	58.6±0.0	128.5±0.0
	Right monthly 1	3111.4±52.6	1.0±0.1	113.8±0.4	36.9±0.5	186.6±0.7	304.5±1.9
	Right monthly2	2408.0±0.0	0.9±0.0	97.1±0.0	35.9±0.0	126.8±0.0	303.2±0.0
	<63µm Bed	2729.7 ±172.9	1.8±0.1	223.6±7.7	32.1±1.1	341.6±51.7	586.8±17.6
	63µm-2mm Bed	499.4± 41.6	0.4±0.1	27.3±0.1	12.2±2.9	149.0±21.8	138.4±10.8
	<63µm Bank	2888.6± 31.3	3.5±0.0	213.6±3.2	46.0 ±0.9	687.9±15.7	831.5±14.9
	63µm-2mm Bank	1026.8± 11.1	1.3±0.1	67.7±3.1	16.5±0.3	238.5±10.2	272.9±6.2
November, 2011	Left monthly 1	1733.6± 8.5	1.9±0.1	104.4±3.0	31.9±0.4	92.0±0.1	237.9±4.7
	Left monthly 2	1845.4± 61.8	2.0±0.0	139.9±1.4	28.7±0.4	114.4±2.1	305.8±2.9
	Right monthly 1	1981.1± 22.2	2.0±0.1	123.1±8.5	51.0±3.9	106.1±7.2	281.6±10.5
	Right monthly2	2021.6± 1.0	2.3±0.0	167.4±0.7	32.1±0.3	138.7±1.2	339.4±4.3
	<63µm Bed	1085.8± 187.8	1.6±0.1	165.7±26.5	17.5±0.7	150.0±40.1	306.2±44.3
	63µm - 2mm Bed	534.2±166.1	0.7±0.0	25.6±8.6	7.7±0.8	36.9±2.2	84.8±4.2
	<63µm Bank	2799.6±33.7	6.2±0.1	177.0±2.0	43.5±0.7	650.9±8.0	779.9±12.3
	63µm-2mm Bank	1121.2± 5.7	2.7±0.0	67.0±1.4	17.7±0.3	265.1±5.6	314.8±1.8
December, 2011	Left monthly 1	4425.3± 0	3.7±0.0	415.0±0.0	41.6±0.0	312.5±0.0	826.6±0.0
	Left monthly 2	3808.6± 0	3.8±0.0	266.6±0.0	49.5±0.0	310.7±0.0	830.7±0.0
	Right monthly 1	874.7±10.3	1.2±0.0	53.9±1.9	14.6±0.2	106.7±14.5	186.1±4.1
	Right monthly2	1875.1± 0.0	2.2±0.0	115.9±0.0	31.2±0.0	182.8±0.0	386.6±0.0
	Bed <63µm	1817.8±34.0	3.1±0.4	177.0±3.1	28.6±1.0	207.1±4.6	388.6±9.0
	Bed 63µm- 2mm	406.9±35.0	0.8±0.1	30.2±11.1	8.8±1.2	43.7±8.4	164.3±46.2
	Bank <63µm	2223.0± 115.1	4.5±0.3	162.6±5.7	37.3±2.6	601.2±42.5	639.5±45.2
	Bank 63µm-2mm	1016.4± 8.6	2.1±0.1	66.7±1.5	16.4±0.2	248.6±4.8	281.3±5.5

Table 9.2 The total concentration (± SD) of phosphorus and heavy metals in storm event sediment samples (May, 2012) (n=3)

	Sediment compartment	P, mg/kg	Cd, mg/kg	Cu, mg/kg	Ni, mg/kg	Pb, mg/kg	Zn, mg/kg
Storm sample (May 2012)	Left after storm 1	2546.1±250.1	15.2±1.6	215.0±19.6	34.45±3.6	257.0±25.2	623.7±56.8
	Left after storm 2	2964.1±78.9	20.1±0.6	281.4±4.3	43.5±0.5	348.2±3.1	879.0±8.6
	Right after storm 1	3173.9± 47.1	20.8±0.6	275.9±6.3	43.0±1.1	327.4±6.0	830.7±7.7
	Right after storm 2	3208.1±115.0	19.2±2.1	260.0±3.4	40.9±0.8	332.1±2.3	740.3±7.4
	Bed <63μm	1006.0± 53.6	<	161.9±7.9	26.0±1.4	178.4±6.7	324.7±6.7
	Bed 63μm-2mm	391.0± 58.07	<	38.1±14.5	12.3±0.0	70.0±14.3	108.0±12.0
	Bank <63μm	1893.7± 23.8	33.80±0.8	170.8±2.7	43.6±1.0	617.3±6.9	679.4±5.8
	Bank 63μm-2mm	833.5± 54.4	13.80±0.5	63.3±2.1	17.2±1.3	243.0±4.5	265.3±1.7

< below the limit of detection

There was a significant positive correlation ($p<0.01$) between the concentration of P and the concentration of all the metals (Table 9.3).

Table 9.3 Spearman correlation between total P concentration and total metal concentration in sediment

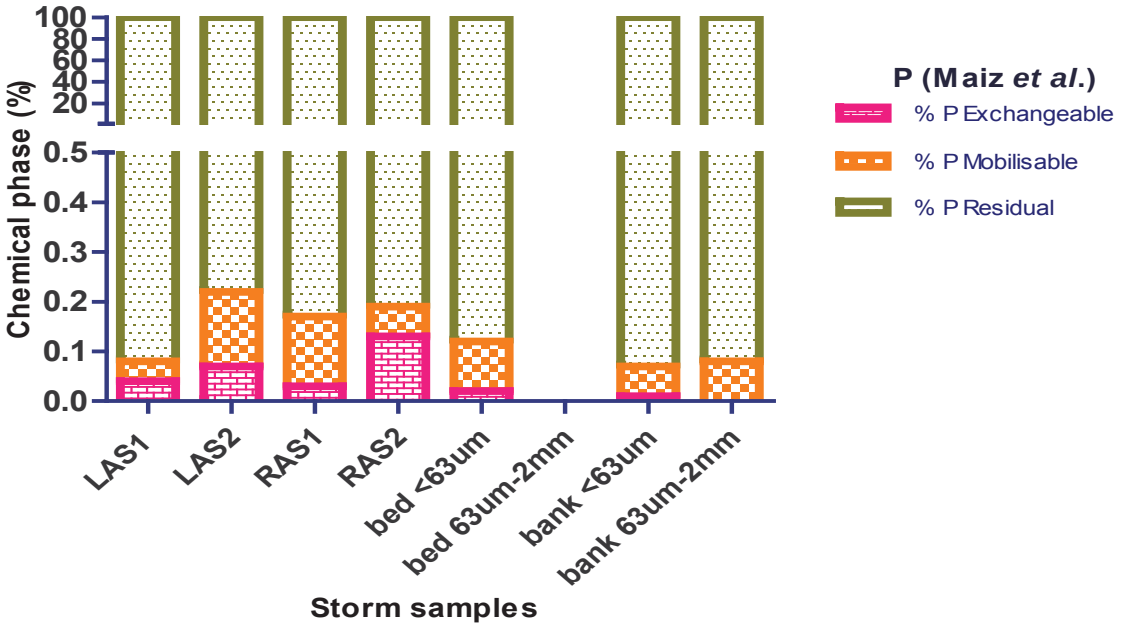
Spearman correlation	Cd	Cu	Ni	Pb	Zn
P (n=24)	0.52**	0.74***	0.92***	0.54**	0.74***

** $p<0.01$, *** $p<0.001$

9.2 Sequential extraction of phosphorus

9.2.1 Maiz *et al.* sequential extraction of phosphorus in sediment from storm event

The sequential extraction of phosphorus from sediment has often shown that the phosphorous is associated with the residual, Fe/Mn and organic matter components of sediment (Chakrapani and Subramanain, 1996). The chemical speciation of phosphorus using the Maiz *et al.* (1997) method was determined using the storm event samples (Figure 8.1). Approximately 99% of the total phosphorus was associated with the residual fraction. The other 1% was retained in the exchangeable and mobilisable phases. This suggests the majority of the phosphorus was not readily bioavailable. There was no P in the 63µm – 2mm fraction of the bed sediment (Figure 9.1).

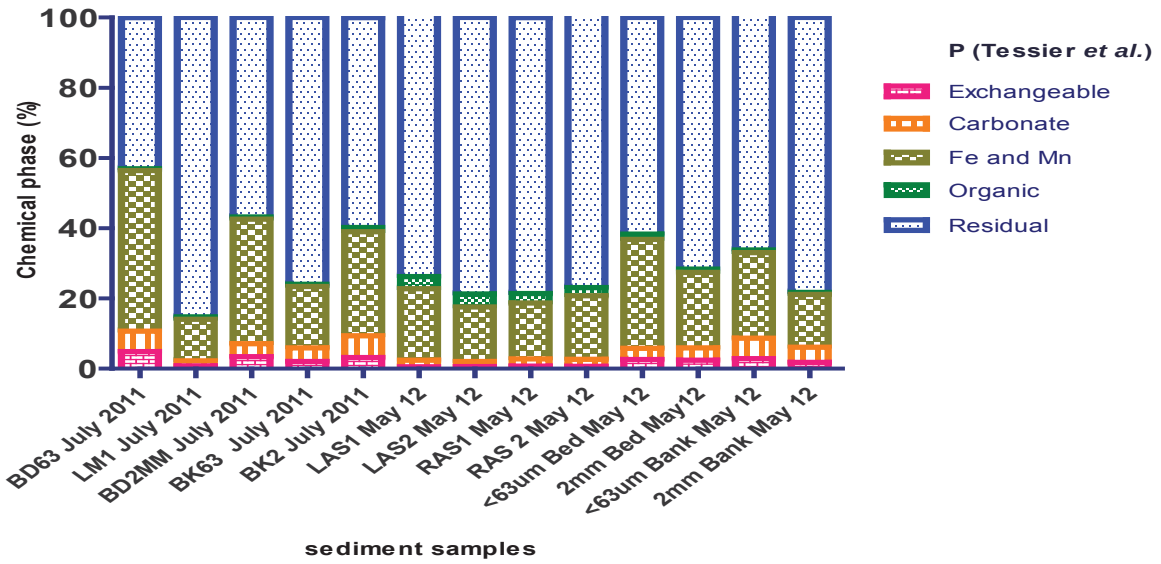


LAS - left after storm, **RAS**-right after storm

Figure 9.1 The mean percentage of phosphorus in storm sediment samples (May 2012) using Maiz *et al.* (1997) sequential extractions method (n=3).

9.2.2 Tessier *et al.* (1979) sequential extraction

The chemical speciation of phosphorus using the Tessier *et al*. (1979) method varied with sediment compartment. Unlike the Maiz *et al*. (1997) method, majority of the phosphorus was not only associated with the residual phase but also with the Fe/Mn phase (Figure 9.2). About 40-80% of phosphorus was retained in the residual fraction, and between 11-45% was retained in the Fe/Mn phase. The percentage of the bioavailable phosphorus was higher in the bed and bank sediment compared to the suspended sediment.



LAS - left after storm, **RAS** - right after storm

Figure 9.2 The mean percentage of phosphorus in sediment using Tessier *et al.* (1979) sequential extractions method (n=3 of replicate analyses).

The concentration of P tends to be higher in the bed and bank sediment compared to the suspended sediment. Like most of the heavy metals (Cd, Ni, Pb and Zn), phosphorus was mainly associated with the Fe/Mn and residual phase. The association of P in sediment follows the order: Residual>Fe/Mn>carbonates>exchangeable>organic. There was a significant correlation (P<0.001) between the concentration of P in the residual phase and the concentration of all the heavy metals in the residual phase (Table 9.4).

Table 9.4 Spearman correlation between the concentrations of P in the residual phase with the concentration of all the heavy metals in the residual fraction

	Cd	Cu	Ni	Pb	Zn
P	0.93***	0.98***	0.87***	0.86***	0.92***

*** p<0.001

The difference in the concentration of P using the Maiz *et al*., 1997 and the Tessier *et al.,* 1979 method was similar to that obtained with heavy metals (Chapter 8). The concentration of bioavailable phosphate was higher in the Tessier *et al.* (1979)

sequential extraction method. As with the metals, most of the P in sediment appeared not to be bioavailable using the Maiz *et al.* (1997) method but between 20-60% of P was bioavailable using the Tessier *et al*. (1979) sequential extraction method. There was no consistency in the concentration of P between the bed, bank and suspended sediment, but the total concentration of P tends to be higher mainly in the suspended sediment with the Tessier *et al*. (1979) method.

9.3 Discussion

Phosphorus (P) tends to behave similarly to the heavy metals in the Ravensbourne sediment though P had a higher concentration compared to the selected metals. A similar pattern of association with sediment was found using both the Maiz *et al*. (1997) and the Tessier *et al.* (1979). Iron and Mn hydrous oxides are significant components for the absorption of P in the aquatic environment, and are likely to be the reason for P association with it (Chakrapani and Subramanain, 1996). The significant relationship between the total metal concentration and P, and the significant relationship between concentration of P in the residual phase and the concentration of all the heavy metals in the residual phase confirm that together with organic matter and Fe/Mn hydroxides, P is likely to be a major sink for these heavy metals with the possibility that it reacted with metals to form insoluble metal phosphates (Cao *et al*., 2003). Similar results of metal association with phosphate have been published by Houba *et al*. (1983). A significant proportion of the metal in the residual phase may be in the form of a precipitates with phosphorus. Since phosphate is a particular contaminant problem in many UK Rivers, and is a significant reason for rivers failing good quality status in WFD assessments (Doody *et al.,* 2012) the formation of phosphate metal precipitates may be a common fate of heavy metal pollutants in rivers.

The predominantly Clay minerals identified in the Ravensbourne sediment such as illite [$(KAl_2\ (Si_3Al)O_{10}(OH)_2$], muscovite [$K(Al.88FeO_{12})(Si_3Al)O_{10}(OH)_2$], calcite [$CaCO_3$], kaolinite [$Al_4(OH)_8(Si_4O_{10}$], dolomite [$CaMg(CO_3)_2$], montmorillonite [$(Al,Mg)_2Si_4O_{10}(OH)_2.4H_2O$] and goethite [(FeO(OH)] did not suggest any mineralogical source of P (Figure 6.4 - Figure 6.7, Chapter 6). This suggests that the sources of P in this urban river are likely to be mainly from anthropogenic such as

fertilizer, misconnections; combined sewage overflows (CSOs). Significant sewage pollution was reported in Bromley Common (upstream of the sampling location) in June 2010 (Table 3.3, section 3.8), and could possibly be a continued source of P in the Ravensbourne.

SECTION 3

Conclusion and Recommendations

Conclusion

The European Water Framework Directive (WFD) is the main driver for sediment monitoring because of the important role sediments play in water quality, especially as a source of contaminants for the water column in aquatic environments (Bilotta and Brazier, 2008, Taylor and Owens, 2009). The development of analytical procedures to determine sediment metal concentration and of sediment sampling techniques to monitor environmental quality standards (EQS) remains crucial for the effective management of river quality. However, the monitoring of contaminated sediment is complex due to the variations in the physical and geochemical characteristics of sediments (Page *et al.,* 2012). The problems associated with sampling different river sediment compartments in order to monitor compliance with any future UK sediment EQS presents a challenge particularly with respect to the most suitable sediment compartment to sample and the appropriate sediment particle size to use.

The <63μm sediment fraction is widely reported to have the greatest impact on aquatic biology not only because high concentrations of metals are often associated with it, but also because it is the sediment fraction that serves as a food for benthic organisms (USEPA, 2007, Luoma and Rainbow, 2008; Strom *et al.,* 2011). Environmental quality standards should be able to capture the sediment fraction posing greatest risk. The <63μm fraction has been suggested as the appropriate fraction to monitor for EQS, but this might ignore the contribution of metal load by larger fractions in rivers with gravel beds like the Ravensbourne. However, it is the ecological relevance of heavy metals retained in larger fractions that is at issue when considering setting EQS and stipulating the sediment fraction used for monitoring. There is a major challenge when using the <63μm sediment fraction for monitoring purposes in rivers such as the Ravensbourne. Collecting sufficient sediment mass for laboratory analysis was difficult from both the bed and suspended sediment. Although, replicate sampling tubes were installed at the sampling location in order to obtain additional sediment samples, the mass of suspended sediment was often still not sufficient for full analysis. This was probably related to the low river velocity and the nature of gravel bed sediment but is likely to be a common problem in many small rivers particularly in urban environments. The collection of suspended sediment over a longer period of time rather than the usually monthly sampling could

allow sufficient mass of sediment to be trapped in the integrated suspended sediment sampler and provide sufficient mass for adequate for laboratory analysis. The Fraunhofer Institute (2002) argued that suspended sediment should be used for sediment monitoring because it represents the most recent sediment influx into the river system and can be used to study recent contamination trends. This though assumes that it is possible to collect sufficient sediment mass, which may not always be the case. This study on the Ravensbourne suggests that suspended sediment will not be the best sediment compartment to sample for shallow rivers with gravel beds.

Sampling the bed sediment for monitoring may present similar problems. Bed sediment sampling of gravel bed rivers to ensure sufficient mass of the <63μm sediment fraction for analysis is likely to require the collection of a relatively large number of sub samples from different sections of the river. This makes sampling laborious and time consuming. The <2mm (<63μm + 63μm-2mm) sediment fraction appears to be the most appropriate particle size fraction to sample for a standardized and widely applied sediment monitoring programme for determining compliance with environmental quality standards both for gravel and non-gravel bed sediment. This is an ecological and realistic fraction in terms of biological exposure and collecting sufficient sediment mass for analysis (Chapter 7).

The concentration of metals clearly showed variations with metals and sediment compartment. The <63μm fraction of the bank sediment retained higher concentrations of all the heavy metals compared to the same fraction for the bed sediment and suspended sediment compartments in most of the sampling months. This is probably due to the larger surface area, higher organic matter content and the different mineralogy of the bank sediment (Chapter 6). There was no significant difference between the metal concentrations in the <63μm bed sediment and suspended sediment. This again tends to suggest that the bed is a suitable compartment to monitor to ensure compliance with any EQSs because it is the sediment compartment that is always in contact with benthic organisms and sufficient mass of sediment can be obtained. The concentration of metals in each of the integrated tube samplers positioned differently in the river did not show significant ($p>0.05$) variation throughout the sampling period provided the integrated tube samplers are located with a straight section of the river.

Although the mineralogy of the bed, bank and suspended sediments showed similarity in the type of clays minerals retained, the percentage of each mineral was different. The suspended sediment contained a higher percentage of clay minerals which are mainly associated with the smallest sediment fraction (<63µm), followed by the bank sediment. The bed sediment contained higher percentage of the non-reactive quartz, particularly in the 63µm – 2mm sediment fraction, which in addition to its small surface area, are probably the major reasons for the low metal concentration in the 63µm – 2mm bed sediment fraction (Chapter 6). The bed and suspended sediment are the most widely used sediment compartments for sediment monitoring (Lee *et al.,* 2003; Ballantine *et al*., 2009). The sampling of the bed sediment seems to have more advantages compared to sampling the suspended or bank sediment, not only because it provides habitat for benthic and aquatic organisms, but sufficient sediment mass can be collected (either from collecting several sub samples of the gravel bed sediment to obtain sufficient mass of the <63µm fraction or by using the <2mm (<63µm + 63µm-2mm)).

The concentration of heavy metals in the bed, bank and suspended sediment of the Ravensbourne exceeded the draft UK sediment quality guidelines for most of the sampling periods (Chapter 7). Monitoring sediment for heavy metals presents a particular dilemma since metals persist in the environment and their concentrations partly reflect historic pollution (Horowitz, 1991, Luoma and Rainbow, 2008). The argument that suspended sediment measures the most recent influx of metals into a river (Fraunhofer Institute, 2002) may be appropriate as part of the monitoring of water quality but it would fall well short of the reality of the potential exposure to benthic organisms. Metal concentrations in both ingestible and non-ingestible sediment fractions may easily exceed sediment guidelines; the question may be whether this metal is actually bioavailable? The results of the sequential extraction for the two sediment size fractions indicated that some of the metal is indeed bioavailable although the amount varied with extraction technique (Chapter 8). Environmental quality standards based on the bioavailable fraction of metal in sediment would provide information on the ecological risk of sediment compared to the total metal concentrations that might overprotect the aquatic environment. A revision of the draft UK sediment quality guidelines based on the outcome of toxicity tests to establish the no effect concentrations of metals on benthic organisms may

be appropriate. Most sediment guidelines are based on annual average concentrations, but these are likely to mask any seasonal variations, variation as a result of storm events and any point source pollution that was not controlled at source which is likely to have significant impact on aquatic biology over a short period of time. The sampling year was marked in general by low rainfall; more variation in rainfall with season may result in differences in sediment metal concentrations particularly in the bed and suspended sediment.

The variation in outcome with the analytical technique used for estimating metal concentrations was another important factor that affected sediment monitoring. The use of strong concentrated acid mixtures with or without hydrofluoric (HF) acid is probably not necessary for metal monitoring since it releases metals retained in silicates (Chapter 7). These are not bioavailable and do not pose toxicity threat to benthic and aquatic organisms. The results for total metal extraction in sediment using the aqua regia ($1HNO_3$:3HCl) and $HF/HClO_4/HNO_3$ indicated that there were no significant difference between the two extracting solutions (Chapter 7). However, the different results obtained from using two different sequential extraction methods further confirm the need for the standardization of analytical techniques. This is particularly important if EQSs are set on the bioavailable fraction of sediment metals rather than on the total metal concentration. The Tessier *et al*. (1979) is the most widely used technique and gives detailed description of heavy metal phases. It, however, takes a longer time to complete the analysis than the Maiz *et al.* (1997). Excessive analytical complexity and time are a considerable disadvantage for routine monitoring programmes. This problem may be minimised if the frequency of sediment sampling is reduced from monthly to quarterly sampling for example. Certainly an annual average EQS would make sequential extraction procedures possible, although this would depend on the number of sampling locations and repeat samples. Establishing a monitoring programme may involve an initial period of sampling to establish how variable metal concentrations are with time at a particular site in order to select an appropriate monitoring frequency. Sequential extraction offers the possibility of identifying the bioavailable concentration of metals. This may be a more appropriate concentration to use for setting sediment quality guidelines and ultimately standards. The difficulty is that different sequential extraction methods result in substantially different estimates of the bioavailable

fractions. If the bioavailable fraction of metals is to be used in setting EQSs then it is important undertake toxicity studies for benthic organisms exposed to different bioavailable metal concentrations determined by a variety of sequential extraction methods. EQSs could then be set on the basis of a standard sequential extraction technique to be used for sediment monitoring.

The pollution contribution from pore water is not mentioned in the WFD and not included in most water monitoring programmes. As clearly indicated in this study, sediment pore waters contain high concentrations of dissolved free metal ions that are likely to be released into the water column and are possibly bioavailable to aquatic organisms (Strom *et al.*, 2011). There have been suggestions on using the concentration of heavy metals in pore water for regulatory purposes instead of sediment quality guidelines because the concentrations of metals in pore water are readily bioavailable to benthic organisms (Carr *et al*., 2001). However, the effectiveness of sampling pore water, the extraction methods used in analysis and collecting sufficient volume of pore water for analysis often remains a challenge.

Finally, of the three sediment sampling techniques used in this study - the Van Veen grab (bed sediment), hand trowel (bank sediment) and time integrated suspended tube sampler (suspended sediment), the hand trowel and the Van Veen grab sampler were the most reproducible, economical and easy-to-use sampling methods for sediment.

A comparison of the advantages and disadvantages of sampling the suspended, bed and bank sediment compartments for environmental quality monitoring from this study are summarised (Table 10).

Table 10 The advantages and disadvantages of sampling the different sediment compartments using this study

	Advantages	Disadvantages
Bed sediment	**1.** The mass of sample collected was sufficient for chemical analysis in gravel bed rivers if the <2mm particle fraction was sampled. **2.** It provides habitat for benthic and aquatic organisms and the physical and chemical characteristics are likely to have a strong impact on the aquatic environment. **3.** It was easy to sample using the Van Veen grab **4.** It allowed better comparison of data because more research work on sediment has been carried out with the bed sediment **5.** It can be used to study historical and recent contaminants in rivers	**1.** It was difficult to collect enough of the <63µm material in gravel bed sediment for chemical analysis.
Suspended sediment	**1.** It can give information on recent sources of contaminants in the aquatic sediment. **2.** There were less variation with particle size (mainly <63µm fraction) compared to the bed and bank sediment.	**1.** The mass of suspended sediment collected was not always adequate for laboratory analysis. **2.** Most of the sampling methods (integrated tube sampler and bulk sediment/water mixture collection) were time consuming **3.** Largely dependent on river velocity and catchment geomorphology
Bank sediment	**1.** Adequate mass of sample was collected for laboratory analysis. **2.** It was easy to sample using the hand trowel	**1.** There were limited study with respect to sediment quality compared to the bed and suspended sediment **2.** Aquatic and benthic organisms are not always exposed to metals associated with this compartment

Recommendations

Having studied the problems associated with sampling different river sediment compartments in order to monitor compliance with any future UK sediment environmental quality standards (EQS), the following recommendations are suggested based on the findings from this study.

- ✓ Although, the <63µm fraction is widely suggested as the most suitable sediment fraction to use for sediment monitoring and in setting any future sediment quality standards, collecting sufficient mass for sediment monitoring in the bed and suspended sediment of the Ravensbourne River was not always possible. The <2mm fraction should be used as an alternative where collecting sufficient mass of the <63µm sediment fraction presents a challenge, particularly in gravel bed rivers and rivers with low sedimentation rate.

- ✓ The bed sediment appears to be the most suitable sediment compartment to sample using either the <63µm or the 63µm-2mm fraction compared to the bank and suspended sediment. This is because it is the sediment compartment that provides habitat for benthic organisms and therefore is constantly in contact with them. It is possible to obtain sufficient mass of sediment, particularly the <2mm fraction, for analysis in both gravel and non-gravel bed rivers.

- ✓ Sediment sampling and monitoring can be tedious and time consuming. The sampling frequency for any future sediment sampling programme in rivers with low sedimentation rates such as the Ravensbourne could be reduced to every two months or quarterly, not only to allow sufficient time for suspended sediment to be trapped in the integrated tube sampler, but also because there was no significant difference between the concentration of metals between the monthly sediment samples collected. This suggests that limited sampling periods should not affect the reliability of monitoring unless there is point source pollution incident. An initial sampling programme to determine the best monitoring frequency for a particular sampling sight is recommended.

- ✓ There is need for a standardized method for studying total metal concentration and metal speciation in sediment. The results from this study showed that the total metal concentrations in sediment do not vary with extracting solution for the Ravensbourne sediment. Hence the aqua regia method which involves the use of less harmful reagent and is also the method used by the Environment Agency would be recommended for future study.

- ✓ Setting future sediment quality standards using the bioavailable fractions should be supported by sediment toxicity tests due to the variations in results from different sequential extraction analytical techniques.

- ✓ There is a need to review the UK draft sediment quality guidelines for total metal concentration in sediment adopted from the Canadian threshold effect level (TEL) and predicted effect level (PEL) since the concentration of heavy metals in the bed, bank and suspended sediment exceeded the draft UK sediment quality standards. It may be more appropriate to set the standards in terms of the bioavailable fraction of the metals, which is the fraction that is likely to be released into the water column and have impact on the river biota. This will ignore the metal concentration retained within the mineral lattice of sediment samples, which are unlikely to be released to the environment or result in exposure benthic organism to metals.

Future work

The following work are recommended for future study

1. To sample different sections of the Ravensbourne River, preferable a non-gravel bed section, to compare results with those obtained in this study.
2. To carry out similar study using the same sampling techniques in another London river with a higher river discharge and different characteristics from the Ravensbourne River in order to compare results with those obtained in this study.
3. To standardize a sequential extraction technique, linking the results for the bioavailable fractions with sediment toxicity tests.

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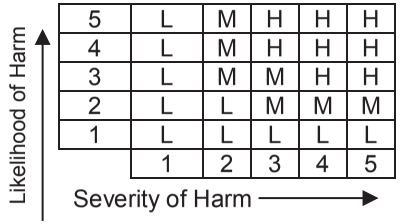
APPENDICES

University of Westminster

General Risk Assessment

Employee: (if applicable)	Ngozi Mokwe-Ozonzeadi
Department / School:	Life Science
Location:	Ravesbourne River, Ladywell field. South East of London.
Activity Assessed:	Sediment Sampling PhD research project
Assessment Date:	
Review Date:	
Assessor(s):	

Risk Factors and Ratings identified are specific to the activity and may change. This general assessment form may identify other specialist assessments that are required i.e. Manual Handling, Display Screen Equipment, Noise, Contact the Health and Safety Unit for further advice



Using the guidance overleaf and chart above; Look across from appropriate 'likelihood' score and up from appropriate 'severity' score to see if risk is 'High', Medium', or 'Low'.

Activity	Hazard	Features affecting risk rating	Likeli-hood (1-5)	Severity Rating (1-5)	Risk Rating (L,M,H)	Existing Controls	Revised/recommended controls (to further minimise risk)	Implementation Date / Action by
Going to Ladywell field	Driving	Major Injury or fatality of the Driver, passengers and commuters	2	4	M	• Use Seat Belts, Serviced car regularly MOT certificate Full Drivers Licence	• Experienced and Safe Driver	
Putting hands in the water to collect sample	Potential chemical and bacteriological hazard	Skin infection of field personnel	4	3	H	• Wear fitted gloves • Wash hands with clean waters after sampling	• Used tight fitted gloves to avoid water entering from the ends of the gloves	

Putting out field equipment and collecting samples	Working alone	Danger of robbery, abuse or death to field personnel	2	4	M	• Inform Director of Studies (DoS) and supervisors when sampling • Check in at pre-arranged times by mobile phone with DoS and supervisors • Work in pairs as much as possible	• Work during the day when the weather is bright and people are in the park	
Access to river	Trip and fall	Major injury to personnel	5	3	H	• Wear suitable clothing and footwear • Do not climb anywhere unsafe or enter potentially dangerous areas • Only enter river during period of low flow • Only walk and sample at a suitable location within a suitable distance from entrance/exit • Suitable Footwear and clothing must be worn	• If water level is above 0.5 m deep or flow rate greater than 0.5 m second do not enter the river	
Sample collection	Carrying and working with sampling equipment	Minor injury/ cut	2	1	L	• Always read through the safety instruction in the manufacture's manual • Carry equipment in a safe manner	If equipment are too much or heavy to carry, use suitable equipment to lift and carry them or get extra help from somebody.	
Sample collection	Weather	Rainfall, storm, snow heatwave or flood	3	4	H	• Always get the weather forecast before going out to collect samples. • Carry appropriate wears to fit weather- brolly, wellies, raincoat, winter clothes, etc/	Always get weather forecast before going out to the field	

Guidance on how to complete this form:

1. Type in details of potential hazard arising from task or work activity in first column
2. Consider people likely to be at risk of harm i.e. staff / clients / visitors / young people / expectant mothers
3. Under current controls: list current management guidance / safety instructions / safety precautions / maintenance procedures / physical controls

4. **Severity of Harm**:
   1 = minor injury (cuts, bruises etc. unlikely to result in absence or lasting harm)
   2 = moderate injuries (likely to result in 1 - 3 days absence)
   3 = major injuries (likely to result in 3 or more days absence and notifiable to HSE)
   4 = death
   5 = multiple deaths

5. **Likelihood**:
   1 = feasible but unlikely (less then once every five years)
   2 = rarely (once in every 1 - 5 years)
   3 = infrequently (between quarterly and annually)
   4 = regularly (between weekly and once a quarter)
   5 = frequently (daily or weekly)

Likelihood of Harm						
5	L	M	H	H	H	
4	L	M	H	H	H	
3	L	M	M	H	H	
2	L	L	M	M	M	
1	L	L	L	L	L	
	1	2	3	4	5	Severity of Harm →

6. The matrix above helps to assign the risk as low, medium or high

7. If **HIGH** - immediate action is needed to reduce the risk. Additional or revised controls can then be outlined in the applicable column

   If **MEDIUM** - Action is needed within stated timescales to reduce the risk. Additional or revised controls can then be outlined in the applicable column

   If **LOW** - Review annually or when circumstances change

The box below can be completed if additional resources needed or a change in approach / management guidance needs to be adopted.

Summary of issues and resources implications:

The Manager and employee should sign and date the form below to confirm that they have received, read and understood the risk assessment:

Manager: (Insert name)	Dr Sharron McEldowney	**Employee: (Insert name)**	Ngozi Mokwe-Ozonzeadi
Appointment	Director of Studies	**Signature**	
Signature		**Date**	
Date			

The following details are to be completed by senior management

Details or resources authorised / refused / deferred:

Manager:
(Insert name) _____

Appointment _____

Signature _____

Date _____

Appendix 2 Summary of field data

	Location (meters from bank)	**Depth** (meters)	**Time** (Sec)	**Velocity** (ms^{-1})	**Cross sectional area** (m^2)	**Flowrate/discharge** (ls^{-1})
Sep-10	1m	0.25	53	0.10	2.06	219
	3m	0.28	58			
	6.5m	0.28	65			
	Average	0.27	58			
Oct-10	1m	0.3	39	0.13	1.915	256
	3m	0.25	45			
	6.5m	0.2	55			
	Average	0.25	46			
Nov-10	1m	0.3		0.06	2.04	129
	3m	0.25				
	6.5m	0.25				
	Average	0.26				
Dec-10	1m	0.25		0.06	2.24	135
	3m	0.28				
	6.5m	0.35				
	Average	0.29				
Jan-11	1m	0.25		0.05	1.66	83
	3m	0.2				
	6.5m	0.2				
	Average	**0.22**				
Feb-11	1m	0.5	10	0.62	3.83	2370
	3m					
	6.5m					
	Average					
Apr-11	1m	0.35	48	0.11	2.35	260
	3m	0.27	52			
	6.5m	0.3	68			
	Average	**0.31**	56			
May-11	1m	0.2	54	0.10	2.20	224
	3m	0.35	60			
	6.5m	0.31	68			
	Average	**0.29**	60			
Jun-11	1m	0.3	35	0.15	2.12	320
	3m	0.28	40			
	6.5m	0.25	48			
	Average	**0.28**	41			
Jul-11	1m	0.25	60	0.10	1.61	173
	3m	0.2	55			
	6.5m	0.18	58			
	Average	**0.21**	57			
Aug-11	1m	0.43	44	0.12	2.20	264
	3m	0.25	52			
	6.5m	0.18	59			
	Average	**0.29**	51			

	Location (meters from bank)	**Depth** (meters)	**Time** (Sec)	**Velocity** (ms^{-1})	**Cross sectional area** (m^2)	**Flowrate/discharge** (ls^{-1})
Sep-11	1m	0.4	60	0.10	2.04	196
	3m	0.25	64			
	6.5m	0.15	70			
	Average	**0.27**	64			
Oct-11	1m	0.3	42	0.12	2.681	332
	3m	0.25	58			
	6.5m	0.5	50			
	Average	**0.35**	50			
Nov-11	1m	0.48	62	0.10	2.9874	305
	3m	0.41	54			
	6.5m	0.28	66			
	Average	**0.39**	60			
Dec-11	1m	0.45	34	0.16	2.681	430
	3m	0.4	46			
	6.5m	0.2	36			
	Average	**0.35**	38			

Appendix 3 Particle size analysis

Sample	Span	SSA(m^2g^{-1})	D50 (μm)
LM1 Sept 2010	8.38	1.02	11.85
LM2 Sept 2010	24.88	0.85	17.84
RM1 Sept 2010	3.78	0.58	49.12
RM2 Sept 2010	4.75	0.82	19.11
LM1 October 2010	5.56	0.81	20.68
LM2 October 2010	7.88	0.82	19.87
RM2 October 2010	3.70	0.49	41.95
LM1 November 2010	4.36	0.71	27.86
LM2 November 2010	6.33	1.02	11.69
LM1 Dec 2010	4.82	0.91	14.73
LM1Jan 2011	6.74	0.83	17.4
RM1Jan 2011	6.82	0.74	22.32
RM2 Jan 2011	4.19	0.65	27.09
<63μm Bank Jan 2011	3.79	1.26	10.43
63μm-2mm Bank Jan.2011	3.18	0.71	99.67
<63μm Bank Feb. 2011	9.88	0.91	15.81
63μm-2mm bank Feb 2011	1.99	0.21	191.17
LM1 April 2011	8.03	0.99	16.2
LM2 April 2011	3.41	0.41	77.46
RM1 April 2011	5.06	0.54	38.30
<63μm Bed April 2011	8.31	0.34	36.69
63μm-2mm Bed April 2011	1.77	0.09	465.53
<63μm Bank* April 2011	2.04	1.31	9.42
63μm-2mm Bank April 2011	1.99	0.25	174.05
LM1 May 2011	5.02	1.01	11.63
RM2 May 2011	4.44	0.63	31.24
<63μm Bed May 2011	4.54	1.12	10.54
63μm-2mm Bed May 2011	1.83	0.08	332.81
<63μm Bank May	9.7	1.16	9.98
63μm-2mm Bank May 2011	2.40	0.44	133.12
RM1 June 2011	3.51	0.53	36.10
RM2 June 2011	4.74	0.68	26.64
<63μm Bed June 2011	1.85	0.18	220.88
63μm-2mm Bed June 2011	1.15	0.02	482.56
<63μm Bank June 2011	10.57	0.84	18.75
63μm-2mm Bank June 2011	1.89	0.19	176.65
LM1 July 2011	3.86	0.83	16.80
LM2 July 2011	3.85	1.13	11.39
RM1July 2011	4.07	0.69	23.26
<63μm Bed July 2011	2.56	0.55	126.58
63μm-2mm Bed July 2011	1.49	0.04	437.58

<63µm Bank July 2011	4.44	1.01	13.58
Sample	**Span**	**SSA(m^2g^{-1})**	**D50 (µm)**
63µm-2mm Bank July 2011	2.01	0.24	168.45
63µm bed August	2.94	0.71	21.61
63µm-2mm bed August 2011	2.49	0.26	189.62
August <63µm bank	3.35	1.02	18.1
August 63µm-2mm bank	2.11	0.24	145.41
Sept 63µm-2mm bed	2.07	0.06	505.04
Sept <63um bank	3.01	1.09	13.72
Sept 63µm-2mm bank	1.94	0.25	185.47
Oct 63µm-2mm Bed	2.13	0.06	266.26
Oct bank <63um	3.00	1.08	11.15
Oct 2011 bank 2mm	11.35	1.08	21.21
Nov 2011 bed 2mm	1.51	0.05	402.95
Nov 2011 bank <63um	3.25	1.14	12.13
Nov 2011 bank 2mm	6.00	0.98	19.21
Dec 2011 bed 2mm	1.40	0.02	569.69
Dec 2011 bank <63um	4.59	0.40	52.87
Dec 2011 bank 2mm	1.80	0.16	177.61
May 2012 LAS1	4.14	0.58	33.35
May 2012 LAS 2	4.70	0.64	26.50
May 2012 RAS 1	5.36	0.72	24.54
May 2012 RAS 2	1.87	1.01	13.80
May 2012 <63µm bed	3.16	0.36	60.49
May 2012 2mm bed	1.47	0.02	635.42
May 2012 bank <63um	3.82	1.30	9.73
May 2012 bank 2mm	2.17	0.26	156.75

Appendix 4 Total metal concentration in bed sediment

Bed <63µm	Cd, mg/kg	Cu mg/kg	Ni (mg/kg)	Pb (mg/kg)	Zn, mg/kg
Jan-11	<	85.73	28.30	303.09	276.87
Apr-11	<	176.58	38.02	271.11	464.55
May-11	3.14	197.42	43.30	555.27	713.01
Jun-11	3.57	144.30	23.67	170.26	320.48
Jul-11	2.64	225.52	33.58	235.85	443.72
Aug-11	3.07	298.18	41.51	269.86	529.74
Sep-11	1.24	176.60	26.12	252.58	414.85
Oct-11	1.76	223.60	32.12	341.58	586.83
Nov-11	1.60	165.74	17.49	150.00	306.15
Dec-11	3.09	176.98	28.56	207.08	388.62
May- 12	0.00	161.94	25.96	178.39	324.67

Bed 63µm-2mm	Cd, mg/kg	Cu mg/kg	Ni (mg/kg)	Pb (mg/kg)	Zn, mg/kg
Jan-11	<	19.34	10.03	63.75	85.85
Apr-11	<	28.79	11.02	72.21	114.00
May-11	<	36.16	12.61	118.17	156.77
Jun-11	1.98	52.69	14.55	59.69	134.03
Jul-11	<	24.99	9.39	94.06	114.96
Aug-11	<	30.72	10.06	96.35	143.92
Sep-11	0.34	26.82	9.51	115.91	137.91
Oct-11	0.35	27.30	12.18	149.00	138.36
Nov-11	0.67	25.62	7.68	36.87	84.74
Dec-11	0.79	30.19	8.75	43.70	164.31
May-12	0.00	38.13	4.09	70.02	107.96

Appendix 5 Total metal concentration in bank sediment

Bank <63µm	Cd, mg/kg	Cu mg/kg	Ni (mg/kg)	Pb (mg/kg)	Zn, mg/kg
Jan-11	2.93	159.99	39.96	523.10	636.14
Feb-11	3.87	162.69	39.76	513.76	693.89
Apr-11	3.67	176.91	39.03	641.69	661.17
May-11	3.20	225.06	41.22	562.40	784.45
Jun-11	6.87	159.19	36.41	542.16	643.05
Jul-11	5.16	154.56	38.44	666.85	663.52
Aug-11	5.22	182.09	42.17	679.52	731.02
Sep-11	4.38	197.24	48.01	820.61	809.95
Oct-11	3.46	213.64	45.96	687.90	831.55
Nov-11	6.23	175.97	43.46	650.90	779.88
Dec-11	4.52	162.55	37.31	601.22	639.53
May-12	33.79	170.76	43.55	617.25	679.38

Bank 63µm-2mm	Cd, mg/kg	Cu mg/kg	Ni mg/kg	Pb mg/kg	Zn, mg/kg
Jan-11	1.10	61.34	17.56	204.63	251.31
Feb-11	<	55.29	15.57	196.03	256.11
Apr-11	2.03	71.32	18.62	301.73	315.56
May-11	<	87.34	18.57	239.13	338.78
Jun-11	3.26	59.49	15.43	243.11	279.58
Jul-11	2.44	62.18	18.09	291.24	304.23
Aug-11	2.13	56.89	15.39	246.47	269.78
Sep-11	1.74	69.91	18.06	314.89	307.89
Oct-11	1.31	67.66	16.52	238.54	272.86
Nov-11	2.71	66.95	17.74	265.08	314.75
Dec-11	2.13	66.68	16.43	248.59	281.25
May-12	13.78	63.27	17.23	243.02	265.25

Appendix 6 Total metal concentration in Left monthly suspended sediment

Left monthly 1	Sample ID	Cd, mg/kg	Cu, mg/kg	Ni, mg/kg	Pb, mg/kg	Zn, mg/kg
27/09/2010	LM1 (Sept)	2.02	213.61	29.62	306.09	740.06
27/10/2010	LM1 (Oct)	<	113.61	21.06	206.08	338.28
27/11/2010	LM1 (Nov.)	<	171.50	26.98	223.94	242.22
30/12/2010	LM1 (Dec.)	1.91	227.50	31.17	267.17	724.01
27/01/2011	LM1 (Jan.)	<	182.46	28.90	241.11	626.08
19/04/2011	LM1 (April)	<	136.06	33.26	214.41	509.47
27/05/2011	LM1 (May)	2.08	225.05	39.79	275.29	776.84
27/06/2011	LM1 (June)	5.96	210.73	36.60	269.33	768.17
27/07/2011	LM1 (July)	4.32	258.53	41.25	368.48	861.24
27/08/2011	LM1 (Aug)	1.88	73.70	29.71	66.86	195.92
27/09/2011	LM1 (Sept)	1.19	97.40	35.36	133.10	258.38
27/10/2011	LM1 (Oct)	0.88	109.70	47.49	140.99	289.70
26/11/2011	LM1 (Nov)	1.90	104.36	31.89	92.00	237.91
23/12/2011	LM1 (Dec)	3.71	415.86	41.60	312.54	826.63
05/05/2012	LAS1 (May 12)	15.15	215.89	34.45	257.94	623.70

Left monthly 2	Sample ID	Cd, mg/kg	Cu, mg/kg	Ni, mg/kg	Pb, mg/kg	Zn, mg/kg
27/09/2010	LM2 (Sept)	1.97	211.60	29.14	286.22	890.33
27/10/2010	LM2 (Oct)	<	132.73	24.29	228.46	448.93
27/11/2010	LM2 (Nov.)	1.52	144.33	29.33	224.56	525.44
30/12/2010	LM2 (Dec.)	<	63.91	22.49	111.29	162.14
27/01/2011	LM2(Jan.)	<	81.56	18.98	128.39	201.49
19/04/2011	LM2April)	<	100.07	26.37	126.27	321.95
27/05/2011	LM2(May)	<	244.45	41.10	298.02	825.82
27/06/2011	LM2(June)	5.98	219.49	38.49	275.00	782.33
27/07/2011	LM2 (July)	3.45	229.66	33.50	317.32	639.97
27/08/2011	LM2 (Aug)	3.36	235.81	46.77	297.09	562.41
27/09/2011	LM1 (Sept)2	1.02	99.43	37.51	137.60	266.33
27/10/2011	LM1 (Oct)2	0.43	56.66	26.66	58.60	128.46
26/11/2011	LM1 (Nov)2	1.99	139.92	28.68	114.43	305.82
23/12/2011	LM1 (Dec)2	3.81	266.59	49.59	310.67	830.72
05/05/2012	LAS 2 (May 12)	20.09	281.39	43.48	348.22	879.02

Appendix 7 Total metal concentration in Right monthly suspended sediment

Right monthly 1	Sample ID	Cd, mg/kg	Cu, mg/kg	Ni, mg/kg	Pb, mg/kg	Zn, mg/kg
27/09/2010	RM1 (Sept)	2.17	207.08	29.17	307.59	629.24
27/10/2010	RM1 (Oct)	<	45.06	23.26	64.74	143.91
27/11/2010	RM1 (Nov)	<	49.04	25.49	71.88	149.74
30/12/2010	RM1 (Dec)	<	78.97	24.67	138.68	190.36
27/01/2011	RM1 (Jan)	<	173.00	27.11	221.93	570.76
19/04/2011	RM1 (Apr)	<	73.31	27.70	96.47	235.50
27/05/2011	RM1(May)	<	229.59	34.27	299.46	404.81
27/06/2011	RM1 (June)	5.04	207.49	29.52	261.24	388.61
27/07/2011	RM1 (July)	2.37	118.47	30.98	126.93	204.55
27/08/2011	RM1 (Aug)	3.18	120.32	51.85	98.62	284.59
27/09/2011	LM1 (Sept)2	1.51	254.85	47.00	103.20	229.68
27/10/2011	LM1 (Oct)2	0.94	113.75	36.90	186.56	304.47
26/11/2011	LM1 (Nov)2	2.03	123.10	51.02	106.13	281.62
23/12/2011	LM1 (Dec)2	1.17	53.85	14.64	106.70	186.08
05/05/2012	RAS1 (May 12)	20.82	275.90	42.99	327.36	830.70

Right monthly 2	Sample ID	Cd, mg/kg	Cu, mg/kg	Ni, mg/kg	Pb, mg/kg	Zn, mg/kg
27/09/2010	RM2 (Sept)	2.36	222.75	28.97	313.73	994.56
27/10/2010	RM2 (Oct)	<	150.68	18.81	179.65	207.34
27/11/2010	RM2 (Nov)	1.98	146.54	24.25	249.05	444.37
30/12/2010	RM2 (Dec)	<	47.52	22.17	69.10	140.51
27/01/2011	RM2(Jan)	<	189.37	29.13	239.54	510.86
19/04/2011	RM2 (Apr)	<	77.55	25.11	143.63	285.11
27/05/2011	RM2 (May)	<	215.98	40.51	258.11	549.31
27/06/2011	RM2 (June)	5.86	227.38	33.75	288.21	622.11
27/07/2011	RM2 (July)	3.43	219.62	33.86	303.94	587.88
27/08/2011	RM2 (Aug)	2.47	149.70	33.99	184.12	430.74
27/09/2011	LM1 (Sept)2	1.16	143.81	60.72	141.60	227.17
27/10/2011	LM1 (Oct)2	0.87	97.11	35.87	126.84	303.23
26/11/2011	LM1 (Nov)2	2.33	167.35	32.07	138.68	339.36
23/12/2011	LM1 (Dec)2	2.23	115.88	31.17	182.81	386.61
05/05/2012	RAS 2 (May 12)	19.16	260.04	40.92	332.10	740.26

Appendix 8 Sequential extraction of heavy metals in <63µm bed sediment

	Cadmium, $mgkg^{-1}$			Copper, $mgkg^{-1}$			Nickel, $mgkg^{-1}$			Lead, $mgkg^{-1}$			Zinc, $mgkg^{-1}$		
Bed <63µm	Exchan-geable	Mobili-sable	Residual	Exchan-geable	Mobili sable	Residual	Exchan geable	Mobili sable	Residual	Exchan geable	Mobili sable	Residual	Exchan geable	Mobili sable	Residual
Jan-11	<	<	<	0.87	11.68	73.18	0.05	0.64	27.61	0.17	22.59	280.33	1.42	33.39	242.06
Apr-11	<	<	<	2.57	19.84	154.16	0.28	2.14	35.60	<	0.22	270.89	0.37	31.00	433.18
May-11	0.03	0.62	2.49	1.43	2.37	193.63	0.80	1.88	40.63	0.49	0.93	553.85	5.79	36.11	671.12
Jun-11	<	<	3.57	<	<	144.30	<	<	23.67	<	<	170.26	<	<	320.48
Jul-11	0.01	0.27	2.36	4.34	24.84	196.34	0.58	1.93	31.07	0.49	5.10	230.26	1.64	45.75	396.33
Aug-11	0.01	0.29	2.77	3.24	19.34	275.60	0.74	2.82	37.95	0.23	4.20	265.43	1.63	51.51	476.60
Sep-11	0.02	0.35	0.87	3.76	32.60	140.24	0.56	1.88	23.68	0.28	30.68	221.62	2.82	77.57	334.46
Oct-11	0.02	0.30	1.44	3.50	6.51	213.60	0.99	1.24	29.89	0.64	0.89	340.04	8.67	46.75	531.42
Nov-11	0.69	0.17	0.74	20.98	10.68	134.08	8.93	3.72	4.84	5.17	<	144.83	172.93	31.15	102.07
Dec-11	0.01	0.17	2.91	3.49	18.48	155.01	0.37	1.25	26.94	<	1.55	205.53	1.07	31.19	356.36
May-12	<	<	<	2.81	20.42	138.71	0.17	0.84	24.95	0.00	19.99	158.40	0.64	49.08	274.95

< - below detection limit

Appendix 9 Sequential extraction of heavy metals in 63µm-2mm bed sediment

	Cadmium, $mgkg^{-1}$			Copper, $mgkg^{-1}$			Nickel, $mgkg^{-1}$			Lead, $mgkg^{-1}$			Zinc, $mgkg^{-1}$		
Bed 63um-2mm	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual
Jan-11	<	<	<	0.48	3.94	14.92	0.05	0.17	9.81	0.33	6.27	57.15	0.54	10.70	74.60
Apr-11	<	<	<	0.38	3.57	24.84	0.03	0.29	10.70	0.02	4.76	67.43	0.12	13.59	100.29
May-11	<	<	<	0.44	3.23	32.49	0.20	0.36	12.05	0.08	19.27	98.82	1.68	19.44	135.64
Jun-11		0.05	1.93	0.37	6.19	46.12	0.02	0.17	14.36	0.07	9.04	50.58	0.15	9.00	124.87
Jul-11	<	<	<	0.53	2.80	21.66	0.03	0.16	9.20	0.18	12.99	80.90	0.25	8.48	106.23
Aug-11	<	<	<	0.48	2.96	27.27	0.05	0.19	9.82	0.08	9.02	87.25	0.26	19.61	124.05
Sep-11		0.04	0.30	0.66	2.71	23.44	0.09	0.14	9.29	0.19	6.77	108.94	0.81	9.84	127.26
Oct-11	0.01	0.05	0.29	0.95	3.04	23.32	0.17	0.14	11.87	0.28	5.88	142.85	2.63	12.50	123.24
Nov-11	<	0.05	0.62	0.52	2.92	22.18	0.02	0.11	7.54	0.15	7.80	28.91	0.70	11.15	72.90
Dec-11	<	0.02	0.77	0.71	1.74	27.74	0.05	0.07	8.62	0.20	3.48	40.01	0.68	6.74	156.90
May-12	<	<	<	0.00	2.73	35.40	0.17	0.84	1.36	0.00	7.54	62.48	0.24	11.15	96.57

<-below detection limit

Appendix 10 Sequential extraction of heavy metals in <63µm bank sediment

	Cadmium, $mgkg^{-1}$			Copper, $mgkg^{-1}$			Nickel, $mgkg^{-1}$			Lead, $mgkg^{-1}$			Zinc, $mgkg^{-1}$		
Bank <63µm	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual
Jan-11	0.01	1.20	1.72	1.04	13.34	145.62	0.14	4.34	35.48	0.73	7.49	514.87	0.90	53.22	582.01
Feb-11	0.01	1.56	2.30	0.89	12.64	149.16	0.13	4.67	34.96	0.40	6.37	507.00	0.84	67.22	625.82
Apr-11	0.01	0.73	2.94	0.89	7.19	168.84	0.09	1.11	37.82	0.19	0.15	641.35	0.51	18.61	642.04
May-11	0.01	0.51	2.68	1.81	8.46	214.79	0.35	1.08	39.79	0.41	1.89	560.10	1.12	34.99	748.34
Jun-11	0.01	0.60	6.26	0.91	12.48	145.80	0.10	1.40	34.91	0.36	5.58	536.23	0.68	37.83	604.54
Jul-11	0.02	0.70	4.44	1.26	10.53	142.77	0.16	1.37	36.91	0.55	6.18	660.12	1.05	36.61	625.87
Aug-11	0.01	0.79	4.42	1.72	10.94	169.43	0.24	1.73	40.20	0.35	4.52	674.65	1.05	39.27	690.69
Sep-11	0.02	0.84	3.51	2.21	14.58	180.46	0.28	1.45	46.28	0.72	4.43	815.46	1.36	39.49	769.09
Oct-11	0.05	0.75	2.65	3.42	3.14	207.07	1.34	1.83	42.80	0.78	1.26	685.86	8.39	34.72	788.43
Nov-11	0.02	1.22	4.98	1.95	10.28	163.75	0.27	2.12	41.08	0.68	2.74	647.48	1.87	47.22	730.79
Dec-11	0.01	0.52	3.99	2.02	10.14	150.38	0.22	1.15	35.93	0.38	2.35	598.49	0.90	27.75	610.88
May-12	0.00	9.35	24.44	1.34	12.62	156.80	0.19	1.59	43.77	0.00	8.43	608.82	0.57	51.76	627.05

Appendix 11 Sequential extraction of heavy metals in 63µm-2mm bank sediment

	Cadmium, $mgkg^{-1}$			Copper, $mgkg^{-1}$			Nickel, $mgkg^{-1}$			Lead, $mgkg^{-1}$			Zinc, $mgkg^{-1}$		
Bank 63µm-2mm	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual
Jan-11	0	0.53	0.57	0.64	9.83	50.87	0.08	1.99	15.49	0.53	23.28	180.82	0.68	36.61	214.02
Feb-11	<	<	<	0.57	8.17	46.55	0.09	1.94	13.54	0.21	23.61	172.21	0.70	41.44	213.96
Apr-11	0.01	0.45	1.58	0.55	6.33	64.44	0.10	1.13	17.39	0.18	7.32	294.23	0.70	36.67	278.19
May-11	<	<	<	0.93	7.31	79.10	0.22	0.71	17.64	0.14	4.46	234.54	0.63	29.11	309.04
Jun-11	0.01	0.28	2.93	0.46	7.93	50.69	0.05	0.66	14.68	0.06	19.61	215.86	0.25	23.94	250.40
Jul-11	0.01	0.38	2.05	0.57	9.00	52.61	0.07	0.76	17.26	0.03	28.00	263.21	0.43	27.61	276.20
Aug-11	0.01	0.32	1.81	0.70	7.95	48.24	0.10	0.72	14.57	0.04	26.89	219.54	0.40	24.89	244.49
Sep-11	0.01	0.40	1.33	0.94	10.51	58.45	0.13	0.68	17.26	0.21	32.89	281.80	0.65	28.55	278.68
Oct-11	0.02	0.32	0.96	1.60	6.34	59.72	0.56	0.69	15.27	0.56	14.02	223.96	3.98	33.49	235.39
Nov-11	0.01	0.46	2.24	0.86	7.36	58.73	0.15	0.76	16.83	0.06	20.11	244.91	1.13	29.44	284.18
Dec-11	0.01	0.68	1.44	0.88	21.51	44.29	0.12	1.48	14.83	0.06	48.66	199.88	0.48	53.93	226.84
May-12	0.00	4.84	8.93	0.72	11.03	51.52	0.00	0.83	16.40	0.00	37.02	206.00	0.33	37.34	227.58

Appendix 12 Sequential extraction of heavy metals in suspended sediment

	Cadmium, $mgkg^{-1}$			Copper, $mgkg^{-1}$			Nickel, $mgkg^{-1}$			Lead, $mgkg^{-1}$			Zinc, $mgkg^{-1}$		
Suspended sediment	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual	Exchangeable	Mobilisable	Residual
RM1 Jan 11	<	<	<	1.19	7.58	164.23	0.25	2.75	24.11	0.52	1.92	219.48	1.75	55.33	513.68
LM1 Jan	<	<	<	0.72	4.79	176.95	0.15	2.98	25.77	0.45	1.77	238.89	1.53	55.99	568.55
LM1Apr	<	<	<	1.19	10.37	124.49	2.07	2.16	29.03	0.67	13.53	200.20	84.82	49.66	374.99
LM2 Apr	<	<	<	1.49	7.31	91.27	2.19	1.64	22.54	0.99	7.82	117.47	96.27	45.61	180.08
RM1 Apr	<	<	<	0.98	5.03	67.29	1.94	3.05	22.70	0.39	5.24	90.84	72.81	75.94	86.75
RM2 Apr	<	<	<	2.75	14.85	59.95	2.64	3.22	19.25	1.68	51.10	90.85	131.98	80.88	72.25
LM1 Jul	0.01	0.20	4.12	0.44	0.97	257.12	0.17	0.78	40.31	0.06	0.18	368.23	3.15	20.67	837.42
LM2 Jul	0.02	0.14	3.30	0.59	2.73	226.35	0.24	0.74	32.53	0.15	1.31	315.86	7.94	27.28	604.75
RM2 Jul	0.06	0.04	3.33	2.21	1.10	216.31	0.81	0.84	32.21	0.56	1.41	301.97	36.07	14.87	536.94
LAS1 May	1.11	2.00	12.04	1.40	3.12	211.36	1.02	0.99	32.43	0	0	257.94	46.79	20.32	556.59
LAS2	0.76	2.71	16.61	1.46	3.92	276.01	0.56	1.22	41.70	0	0	348.22	18.99	34.57	825.46
RAS1	0.00	3.27	17.55	1.75	4.24	269.91	0.25	1.21	41.54	0	0	327.36	5.84	42.28	782.58
RAS2	2.36	1.15	15.66	1.63	3.07	255.34	2.00	0.91	38.01	0	0	332.10	106.41	16.45	617.40

<- below detection limit